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Uncommon Transformations of Methyl (1*S*,2*S*,3*R*,4*R*)-2,3-isopropylidenedioxy-5-iodomethyl-2-tetrahydrofurylacetate Initiated by Bases

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Abstract—Methyl (1*S*,2*S*,3*R*,4*R*)-2,3-isopropylidenedioxy-5-iodomethyl-2-tetrahydrofurylacetate prepared in two stages from *D*-ribose acetonide underwent a series of uncommon transformations under the treatment with bases providing the following different products depending on the base applied: methyl 3-(5-acetyl-2,2-dimethyl-1,3-dioxol-4-yl)propionate (DBU), methyl 2,3-isopropylidenedioxy-7-oxabicyclo[2.2.1]heptane-6-carboxylate (*t*-BuOK), methyl {(5*R*)-2,2-dimethyl-5-[(2*R*)-oxiranyl]-1,3-dioxolan-4-ylidene}propionate and methyl-(*E*)-3-{(4*S*,5*R*)-2,2-dimethyl-5-[(1*R*)-(2-oxiranyl)]-1,3-dioxolan-4-yl}-2-propenoate (*t*-BuOK and LDA).

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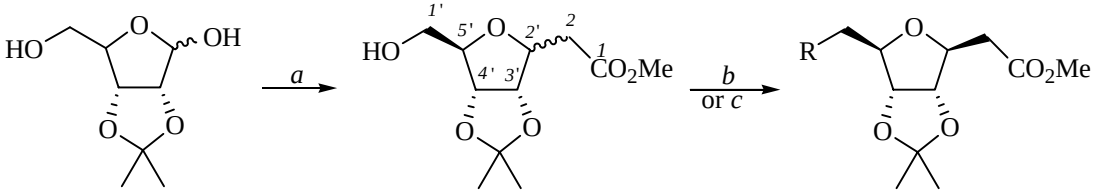
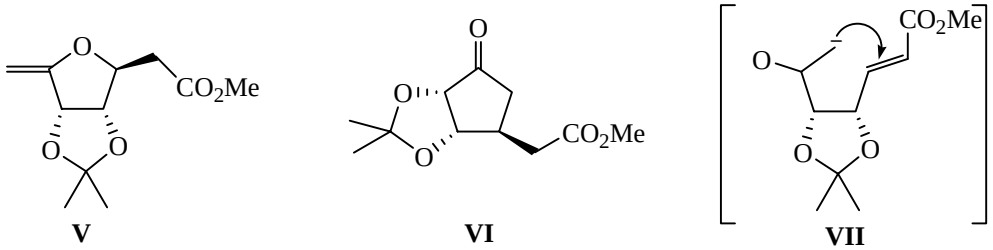
Application of sugars as chiral matrices in a directional synthesis of biologically active compounds is covered in a number of surveys and monographs [1–5]. In this study in order to synthesize optically active polyfunctional cyclopentanoids we investigated some reactions of iodoester **III** prepared from D-ribose acetonide (**I**) [6] via ester **II** [7, 8] occurring with assistance of basic reagents. We planned to perform a new way of carbocyclization of compounds **III** or **IV** into structures **V** and **VI** hoping that under the action of strong deprotonating reagents a retro-Michael decomposition of compound **III** would be initiated providing enolate **VII** capable of repeated intramolecular Michael ring closure involving the more nucleophilic carboanion center and giving as a result cyclopentane derivative **VI**.

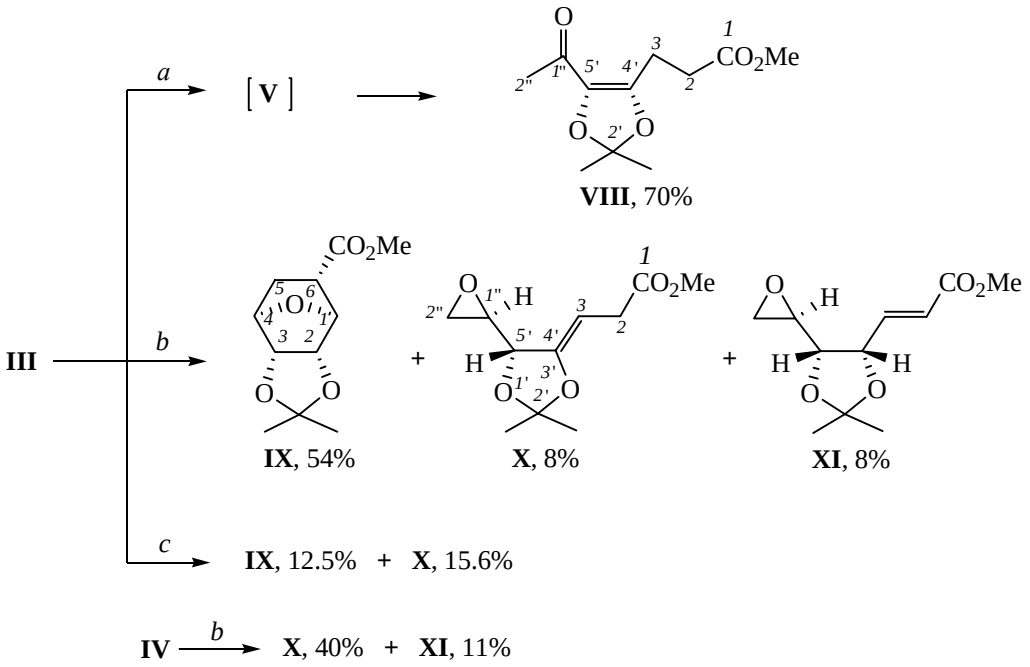


I **IIa** (2'*R*), **IIb** (2'*S*). **III** (R = I), **IV** (R = OTs).



V **VI** **VII**

Reagents and conditions: *a*. $Ph_3P{=}CHCO_2Me$, PhH, 80°C, 2 h (90%); *b*. I_2, Ph_3P, Im, PhMe, 90°C, 1 h (80%); *c*. TsCl, Py, 20°C, 20 h (89%).



Reagents and conditions: (*a*) 2.5 equiv. of DBU, PhH, 80°C, 2 h; (*b*) 1.5 equiv. of *t*-BuOK, THF, 0 → 20°C, 1 h (80%); (*c*) 2 equiv. of LDA, THF, –50°C, 2 h; 0°C, 0.5 h; 20°C, 1 h.

However this attempt failed. The stage of dehydroiodination of iodide **III** with DBU was found to take an abnormal direction. It turned out that the arising *exo*-enol ether **V** under the conditions of reaction rearranged into a more stable derivative of 1,3-dioxol **VIII**. Analogs of this rearrangement were not reported.

On treating iodide **III** with *t*-BuOK in THF we obtained compounds **IX–XI**. As seen, *t*-BuOK converted iodoester **III** not into enol ester **V** but into a number of compounds resulting exclusively from the primary enolyzation of the methoxycarbonyl function. The formation of enol ester **X** is unexpected for it is less thermodynamically preferable than ester **XI**. The fraction of compound **X** was somewhat increased at replacing LDA for *t*-BuOK although the overall yield of compounds **IX** and **X** in this case was also rather moderate. Compound **X** is interesting for attempting intramolecular carbocyclization by Mukaiyma protocol [9]. The yield of this compound at treating with *t*-BuOK tosylate **IV** prepared under standard conditions attained ~ 40%.

Thus we found that methyl (1*S*,2*S*,3*R*,4*R*)-2,3-isopropylidenedioxy-5-iodomethyl-2-tetrahydrofurylacetate easily obtained from D-ribose when treated with DBU, *t*-BuOK, and LDA was converted into different in structure products of rearrangement, intramolecular cyclization and recyclization.

Therefore studying the reaction with basic reagents of methyl (1*S*,2*S*,3*R*,4*R*)-2,3-isopropylidenedioxy-5-iodomethyl-2-tetrahydrofurylacetate obtained from *D*-ribose acetonide we discovered a previously unknown rearrangement and a number of uncommon transformations leading to compounds promising as multipurpose chiral blocks.

EXPERIMENTAL

IR spectra were recorded on spectrophotometers UR-20 and Specord M-80 from films. NMR spectra were registered on a spectrometer Bruker AM-300 at operating frequencies 300.13 (^{1}H) and 75.47 MHz (^{13}C) from solutions in $CDCl_3$ ot CD_2Cl_2, as internal reference served the signals of solvents $CDCl_3$ (CD_2Cl_2) [δ_H 7.27 (5.31), δ_C 77.00 (53.86) ppm]. The reaction progress was monitored by TLC on Silufol plates, spots were visualized by 10% ethanol solution of anisaldehyde containing a little of sulfuric acid [10]. GLC analysis was carried out on a Shimadzu instrument equipped with a glass column 25 m long (sorbent OV-101).

Reaction of acetonide I with methoxycarbonylmethylenetriphenylphosphorane. To a solution of 0.1 g (0.53 mmol) of acetonide **I** in 5 ml of anhydrous benzene was added by portions 0.26 g (0.79 mmol) of methoxycarbonylmethylenetriphenylphosphorane, and the

mixture was stirred at boiling till complete conversion of the initial acetonide (TLC monitoring, 2 h). On evaporating the solvent in a vacuum the residue was subjected to column chromatography on SiO_2 to obtain 0.016 g (12.3%) of ester **IIa** and 0.10 g (76.7%) of ester **IIb** (1:6, GLC) as oily fluids.

Methyl (2*R*,3*S*,4*R*,5*R*)-5-hydroxymethyl-3,4-isopropylidenedioxy-2-tetrahydrofurylacetate (IIa). R_f 0.33 ($CHCl_3$–MeOH, 97:3, average of 3 measurements), $[\alpha]_D^{20}$ +3.3° (*c* 1.0, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1730 (C=O), 3470 (OH). ^1H NMR spectrum (CD_2Cl_2), δ, ppm (*J*, Hz): 1.35 s (3H, Me), 1.50 s (3H, Me), 2.2 br.s (1H, OH), 2.67 d.d (1H, H^{2A}, $^3J_{2A,2'}$ 9.5, $^2J_{2A,2B}$ 13.5), 2.73 d.d (1H, H^{2B}, $^3J_{2B,2'}$ 3.5, $^2J_{2B,2A}$ 13.5), 3.61 d (2H, $H^{1''}$, $^3J_{1'',5'}$ 6.9), 3.70 s (3H, OMe), 4.05 t (1H, $H^{5'}$, $^3J_{5',1''}$ 6.9), 4.35 d.d.d (1H, $H^{2'}$, $^3J_{2',2}$ 3.5, $^3J_{2',3'}$ 4.1, $^3J_{2',2A}$ 9.5), 4.60 d (1H, $H^{4'}$, $^3J_{4',3'}$ 6.1), 4.75 d.d (1H, $H^{3'}$, $^3J_{3',2'}$ 4.1, $^3J_{3',4'}$ 6.1). ^{13}C NMR spectrum (CD_2Cl_2), δ, ppm: 25.06 (Me), 26.33 (Me), 34.67 (C^{2}) 51.95 (OMe), 62.12 ($C^{1''}$), 77.28 ($C^{2'}$), 81.76 ($C^{5'}$), 82.94 ($C^{3'}$), 84.62 ($C^{4'}$), 112.89 ($C^{i\text{-Pr}}$), 171.95 (C^{1}).

Methyl (2*S*,3*S*,4*R*,5*R*)-5-hydroxymethyl-2,3-isopropylidenedioxy-2-tetrahydrofurylacetate (IIb). R_f 0.49 ($CHCl_3$–MeOH, 97:3, average of 3 measurements), $[\alpha]_D^{20}$ –5.2° (*c* 1.0, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1745 (C=O), 3420 (OH). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.34 s (3H, Me), 1.53 s (3H, Me), 2.62 d.d (1H, H^{2A}, $^3J_{2A,2'}$ 6.7, $^2J_{2A,2B}$ 16.0), 2.86 d.d (1H, H^{2B}, $^3J_{2A,2'}$ 4.9, $^2J_{2A,2B}$ 16.0), 3.62 d.d (2H, $H^{1''A}$, $^3J_{1''A,5'}$ 3.9, $^2J_{1''A,1''B}$ 11.7), 3.71 s (3H, OMe), 3.82 d.d (2H, $H^{1''B}$, $^3J_{1''B,5'}$ 3.9, $^2J_{1''A,1''B}$ 11.7), 4.08 q (1H, $H^{5'}$, $^3J_{5',1''}$ 6.9), 4.42 d.d.d (1H, $H^{2'}$, $^3J_{2',2B} = {}^3J_{2',3'}$ = 4.9, $^3J_{2',2A}$ 6.7), 4.53 d.d (1H, $H^{3'}$, $^3J_{3',2'}$ 4.9, $^3J_{3',4'}$ 6.7), 4.74 d.d (1H, $H^{4'}$, $^3J_{4',5'}$ 3.9, $^3J_{4',3'}$ 6.7). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 25.48 (Me), 26.43 (Me), 37.60 (C^{2}), 51.95 (OMe), 62.67 ($C^{1''}$), 80.71 ($C^{2'}$), 81.60 ($C^{5'}$), 83.96 ($C^{3'}$), 84.77 ($C^{4'}$), 114.40 ($C^{i\text{-Pr}}$), 171.30 (C^{1}). Found,%: C 53.88; H 7.52. $C_{11}H_{18}O_6$. Calculated, %: C 53.65; H 7.37.

Methyl (2*R*,3*S*,4*R*,5*R*)-3,4-isopropylidenedioxy-5-iodomethyl-2-tetrahydrofurylacetate (III). To a solution of 1.70 g (6.90 mmol) of alcohol **IIb**, 3.90 g (15.18 mmol) of Ph_3P, and 1.40 g (20.70 mmol) of imidazole in 30 ml of anhydrous toluene was added by portions at 95°C 3.50 g (13.80 mmol) of fine crystals of iodine. The reaction mixture was stirred for 1 h, diluted with an equal volume of ethyl acetate, washed with a saturated water solution of $Na_2S_2O_3$, and with H_2O. The organic layer was dried over Na_2SO_4, filtered, and concentrated in a vacuum, the residue was subjected to column chromatography on SiO_2 (eluent petroleum ether). Yield 1.95 g (79.6%), colorless oily substance, R_f 0.36 (petroleum ether–ethyl acetate, 7:3), $[\alpha]_D^{20}$ –11.9° (*c* 1.0, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1050 (C–O), 1745 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.35 s (3H, Me), 1.55 s (3H, Me), 2.62 d.d (1H, H^{2A}, $^3J_{2A,2'}$ 6.9, $^2J_{2A,2B}$ 15.9), 2.72 d.d (1H, H^{2B}, $^3J_{2A,2'}$ 5.6, $^2J_{2A,2B}$ 15.9), 3.25 d.d (2H, $H^{1''B}$, $^3J_{1''B,5'}$ 5.3, $^2J_{1''A,1''B}$ 10.4), 3.28 d.d (2H, $H^{1''A}$, $^3J_{1''A,5'}$ 4.4, $^2J_{1''A,1''B}$ 10.4), 3.71 s (3H, OMe), 3.91d.d (1H, $H^{5'}$, $^3J_{5',4'} = {}^3J_{5',1''A}$ = 4.4, $^3J_{5',1''B}$ 5.3), 4.30 d.d.d (1H, $H^{2'}$, $^3J_{2',3'}$ 4.0. $^3J_{2',2B}$ 5.6, $^3J_{2',2A}$ 6.8), 4.5 d.d (1H, $H^{3'}$, $^3J_{3',2'}$ 4.0, $^3J_{3',4'}$ 6.7), 4.71 d.d (1H, $H^{4'}$, $^3J_{4',5'}$ 4.4, $^3J_{4',3'}$ 6.7). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 7.11 ($C^{1''}$), 25.52 (Me), 27.34 (Me), 38.12 (C^{2}) 51.84 (OMe), 80.91 ($C^{2'}$), 81.60 ($C^{5'}$), 82.84 ($C^{3'}$), 84.14 ($C^{4'}$), 114.40 ($C^{i\text{-Pr}}$), 171.30 (C^{1}). Found, %: C 37.28; H 4.62; I 35.40. $C_{11}H_{17}IO_5$. Calculated, %: C 37.10; H 4.81; I 35.63.

Methyl (2*R*,3*S*,4*R*,5*R*)-3,4-isopropylidenedioxy-5-*p*-toluenesulfonylmethyl-2-tetrahydrofurylacetate (IV). To a stirred at 0°C solution of 1 g (4.06 mmol) of alcohol **IIb** in 15 ml of anhydrous pyridine was added by portions 1.55 g (8.10 mmol) of TsCl. The reaction mixture was stirred at room temperature for 20 h (TLC monitoring), then it was poured into cold water, and reaction products were extracted into chloroform. The extract was dried over Na_2SO_4 and concentrated in a vacuum, the residue was subjected to column chromatography on SiO_2 to give 1.44 g (89%) of tosylate **IV**, R_f 0.22 (petroleum ether–ethylacetate, 7:3), $[\alpha]_D^{25}$ +4.2° (*c* 1.0, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1100 (C–O), 1190, 1370 (S=O), 1720, 1740 (C=O), 1600 (Ar). ^1H NMR spectrum (CD_2Cl_2), δ, ppm (*J*, Hz): 1.25 s (3H, Me), 1.48 s (3H, Me), 2.40 s (3H, Me^{Ar}) 2.52 t (1H, H^{2A}, $^3J_{2A,2'}$ 7.0, $^2J_{2A,2B}$ 15.9), 2.58 t (1H, H^{2B}, $^3J_{2B,2'}$ 5.6, $^2J_{2B,2A}$ 15.9), 3.62 s (3H, OMe), 4.05–4.07 m (3H, $H^{5'}$, $2H^{1''}$), 4.23 d.d.d (1H, $H^{2'}$, $^3J_{2',3'}$ 4.2, $^3J_{2',2B}$ 5.6, $^3J_{2',2A}$ 7.0), 4.45 d.d (1H, $H^{3'}$, $^3J_{3',2'}$ 4.2, $^3J_{3',4'}$ 6.7), 4.51 d.d (1H, $H^{4'}$, $^3J_{4',1''}$ 3.5, $^3J_{4,'3'}$ 6.7), 7.36 m (3H, $2H^{m}$, H^{i}), 7.76 d (2H, H^{O}, *J* 8.5). ^{13}C NMR spectrum (CD_2Cl_2), δ, ppm: 21.69 (Me^{Ar}), 25.47 (Me), 27.39 (Me), 36.28 (C^{2}), 51.91 (OMe), 69.91 ($C^{1''}$), 81.42 ($C^{2'}$), 81.73 ($C^{3'}$), 82.02 ($C^{5'}$), 84.45 ($C^{4'}$), 114.87 ($C^{i\text{-Pr}}$), 128.25 (C^{O}), 130.29 (C^{m}), 132.79 (C^{i}), 145.65 (C^{θ}), 170.87 (C^{1}). Found, %: C 52.08; H 5.77; S 7.91. $C_{18}H_{24}O_9S$. Calculated, %: C 51.91; H 5.81; S 7.70.

Reaction of iodide III with DBU. *a*. To a solution of 0.2 g (0.56 mmol) of iodide **III** in 5 ml of anhydrous benzene was added 0.11 g (0.70 mmol) of DBU, and the mixture was stirred at 80°C for 2 h. The solution was

concentrated in a vacuum, the residue was subjected to column chromatography on SiO_2 (eluent CH_2Cl_2). We obtained 0.15 g of a mixture of iodide **III** and enol **V** in a ratio 2:1 (^{1}H NMR data).

b. Under similar conditions from 0.2 g (0.56 mmol) of iodide **III** and 0.21 g (1.40 mmol) of DBU in 5 ml of anhydrous benzene 0.09 g (70%) of compound **VIII** was obtained.

Methyl (2*S*,3*S*,4*R*)-3,4-isopropylidenedioxy-5-methylene-2-tetrahydrofurylacetate (V). Colorless oily substance, R_f 0.36 (petroleum ether–ethylacetate, 7:3). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.37 s (3H, Me), 1.47 s (3H, Me), 2.59 d.d (1H, H^{2A}, $^3J_{2A,2'}$ 6.0, $^2J_{2A,2B}$ 11.8), 2.62 d.d (1H, H^{2B}, $^3J_{2B,2'}$ 6.2, $^2J_{2B,2A}$ 11.8), 3.70 s (3H, OMe), 4.26 br.s (1H, $H^{1''A}$), 4.47 m (1H, $H^{3'}$), 4.48 br.s (1H, $H^{1''B}$), 4.62 d.d.d (1H, $H^{2'}$, $^3J_{2',3'}$ 2.0, $^3J_{2',2A}$ 6.0, $^3J_{2',2B}$ 6.2), 5.08 d (1H, $H^{4'}$, $^3J_{4',3'}$ 6.0). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 25.63 (Me), 27.07 (Me), 37.90 ($C^{1''}$), 51.99 (OMe), 79.90 (C^5), 82.47 (C^3), 82.98 (C^4), 86.46 ($C^{1'}$), 161.47 (C^2), 113.54 ($C^{i\text{-Pr}}$), 170.33 ($C^{2''}$).

Methyl 3-(5-acetyl-2,2-dimethyl-1,3-dioxol-4-yl)propanoate (VIII). Colorless oily substance, R_f 0.33 (benzene–ethyl acetate, 95:5, average of 3 measurements). IR spectrum, ν, cm^{-1}: 1050 (C–O), 1710, 1745 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.55 s (6H, Me), 2.23 s (3H, Me), 2.58 t (2H, H^2, $^3J_{2,3}$ 7.5), 2.95 t (2H, H^3, $^3J_{3,2}$ 7.5), 3.70 s (3H, OMe). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 21.49 (C^3), 25.45 ($Me^{i\text{-Pr}}$ and $C^{2'}$), 27.46 ($Me^{i\text{-Pr}}$), 30.88 (C^2), 51.60 (OMe), 115.22 ($C^{i\text{-Pr}}$), 134.90 ($C^{5'}$), 148.08 ($C^{4'}$), 173.50 (C^1), 189.92 ($C^{1'}$). Found, %: C 57.65; H 7.28. $C_{11}H_{16}O_5$. Calculated, %: C 57.88; H 7.07.

Reaction of iodide III with *t*-BuOK. To a solution of 0.2 g (0.56 mmol) of iodide **III** in 6 ml of anhydrous THF at 0°C under an argon atmosphere was added by portions 0.1 g (0.88 mmol) of *t*-BuOK. After stirring for 1 h at room temperature (TLC monitoring) the mixture was filtered and concentrated in a vacuum, the residue was subjected to column chromatography on SiO_2 (eluent benzene–ethyl acetate, 98:2 > 95:5). We obtained 0.07 g (54 %) of compound **IX**, 0.01 g (8%) of enol **X**, and 0.01 g (8%) ester **XI**.

Methyl-2,3-isopropylidenedioxy-7-oxabicyclo-[2.2.1]heptane-6-carboxylate (IX). R_f 0.19 (benzene–ethyl acetate, 95:5, average of 3 measurements), $[\alpha]_D^{20}$ –29.9° (*c* 1.0, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1045, 1090 (C–O–C), 1730 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.28 s (3H, Me), 1.47 s (3H, Me), 1.52 d.d (1H, H^{5endo}, $^2J_{5endo,5exo}$ 13.0, $^3J_{5endo,6endo}$ 9.1), 2.12 d.d.d (1H, H^{5exo}, $^3J_{5exo,4}$ 5.80, $^3J_{5exo,6}$ 9.1, $^2J_{5exo,5endo}$ 13.0), 2.41 d.d (1H, H^{6endo}, $^3J_{6endo,5exo}$ 4.8, $^3J_{6endo,5endo}$ 9.1), 3.72 s (3H, OMe), 4.23 d (1H, H^{2endo}, $^3J_{2endo,3endo}$ 9.5), 4.24 d (1H, H^{3endo}, $^3J_{3endo,2endo}$ 9.5), 4.67 s (1H, H^1). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 25.15 (Me), 25.90 (Me), 27.86 (C^5), 41.96 (C^6), 52.41 (OMe), 78.70 (C^4), 81.29 (C^1), 81.95 (C^2), 82.24 (C^3), 111.85 ($C^{i\text{-Pr}}$), 173.03 [C(=O)]. Found, %: C 58.48; H 6.62. $C_{11}H_{16}O_5$. Calculated, %: C 57.88; H 7.07.

Methyl-{(5*R*)-2,2-dimethyl-5-[(2*R*)-oxiranyl]-1,3-dioxolan-4-ylidene}propionate (X). R_f 0.39 (benzene–ethyl acetate, 95:5, average of 3 measurements), $[\alpha]_D^{20}$ +17° (*c* 1.0, $CHCl_3$). IR spectrum, ν, cm^{-1}: 985 (*trans*-C=C), 1060, 1080 (C–O), 1740 (C=O). ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm (*J*, Hz): 1.38 s (3H, Me), 1.50 s (3H, Me), 2.73 d.d (1H, $H^{2''A}$, $^2J_{2''A,2''B}$ 15.1, $^3J_{2''A'',1}$ 2.5), 2.78 d.d (1H, $H^{2''B}$, $^2J_{2''B,2''A}$ 15.1, $^3J_{2''B,1''}$ 3.8), 3.0 d.d.d (1H, $H^{1''}$, $^3J_{1'',5'}$ 6.3, $^3J_{1'',2''B}$ 3.8, $^3J_{1'',2''A}$ 2.5), 3.09 d.d.d (1H, H^{2A}, $^2J_{2A,2B}$ 15.8, $^3J_{2A,3}$ 7.0, $^5J_{2A,5'}$ 1.5), 3.15 d.d.d (1H, H^{2B}, $^2J_{2B,2A}$ 15.8, $^3J_{2B,3}$ 7.0, $^5J_{2B,5'}$ 1.5), 3.66 s (3H, OMe), 4.31 d.q (1H, $H^{5'}$, $^3J_{5',1''}$ 6.3, $^5J_{5',2A} = {}^5J_{5',2B} = {}^4J_{5',3}$ = 1.5), 4.50 d.d (1H, H^3, $^3J_{3,2A} = {}^3J_{3,2B}$ 7.0, $^4J_{3,5'}$ 1.5). ^{13}C NMR spectrum (CD_2Cl_2), δ, ppm: 25.63 (Me), 26.67 (Me), 30.96 (C^2), 45.11 ($C^{2''}$), 51.96 (OMe), 52.84 ($C^{1''}$), 76.56 ($C^{5'}$), 88.94 (C^3), 113.32 ($C^{i\text{-Pr}}$), 152.06 ($C^{4'}$), 171.61 (C^1). Found, %: C 58.20; H 7.25. $C_{11}H_{16}O_5$. Calculated, %: C 57.88; H 7.07.

Methyl-(*E*)-3-{(4*S*,5*R*)-2,2-dimethyl-5-[(1*R*)-(2-oxiranyl)]-1,3-dioxolan-4-yl}-2-propenoate (XI). R_f 0.30 (benzene–ethylacetate, 95:5, average of 3 measurements), $[\alpha]_D^{20}$ –1.2° (*c* 0.9, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1035, 1070 (C–O), 1745 (C=O). ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm (*J*, Hz): 1.20 s (3H, Me), 1.35 s (3H, Me), 2.47 d.d (1H, $H^{2''A}$, $^3J_{2''A,1''}$ 2.5, $^2J_{2''A,2''B}$ 5.0), 2.63 d.d (1H, $H^{2''B}$, $^3J_{2''B,1''}$ 4.0, $^2J_{2''B,2''A}$ 5.0), 2.68 d.d.d (1H, $H^{1''}$, $^3J_{1'',2''A}$ 2.5, $^3J_{1'',2''B}$ 4.0, $^3J_{1'',5'}$ 7.4), 3.55 s (3H, OMe), 3.64 d.d (1H, $H^{5'}$, $^3J_{5',4'}$ 6.8,$^3J_{5',1''}$ 7.4), 4.72 d.d (1H, $H^{4'}$, $^4J_{4',2}$ 1.7, $^3J_{4',3}$ 5.0, $^3J_{4',5'}$ 6.8). ^{13}C NMR spectrum (CD_2Cl_2), δ, ppm: 25.08 (Me), 27.49 (Me), 46.09 ($C^{2''}$), 49.69 ($C^{1''}$), 51.69 (OMe), 76.71 ($C^{5'}$), 79.08 ($C^{4'}$), 110.10 ($C^{i\text{-Pr}}$), 122.78 (C^2), 141.92 (C^3), 166.17 (C^1). Found, %: C 57.71; H 6.93. $C_{11}H_{16}O_5$. Calculated, %: C 57.88; H 7.07.

Reaction of iodide III with LDA. To a solution of 0.113 g (1.12 mmol) of $i\text{-Pr}_2NH$ in 3 ml of anhydrous THF was added 0.66 ml (1.12 mmol) of 1.7 N solution of

BuLi at –10°C under an argon atmosphere. The reaction mixture was stirred for 0.5 h at –10°C, then it was cooled to –50°C , and a solution of 0.2 g (0.56 mmol) of iodide **III** in 3 ml of anhydrous THF was added dropwise. The mixture was stirred at –50°C for 2 h, at 0°C for 0.5 h, and 1 h at room temperature (TLC monitoring). On cooling the reaction mixture to –25°C 1 ml of saturated NH_4Cl solution was added, and the solution was concentrated in a vacuum. The product was extracted into ethyl acetate, the combined organic extracts were washed with a saturated NaCl solution, and dried over Na_2SO_4. On evaporating the solvent in a vacuum the residue was subjected to column chromatography on SiO_2 (eluent petroleum ether–ethyl acetate, 97:3 > 8:2) to isolate 0.016 g (12.5%) of compound **IX** and 0.02 g (15.6%) of enol **X**.

Reaction of tosylate IV with *t*-BuOK. To a solution of 0.3 g (0.75 mmol) of tosylate **IV** in 7 ml of anhydrous THF was added by portions 0.11 g (0.97 mmol) of *t*-BuOK at 0°C in an argon atmosphere. The reaction mixture was stirred for 0.5 h at room temperature (TLC monitoring), filtered, the filtrate was concentrated, and the residue was subjected to column chromatography on SiO_2 (eluent petroleum ether–ethyl acetate, 95:5) to isolate 0.07 (40%) of enol **X** and 0.02 g (11%) of ester **XI**.

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