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Reaction of Iodolevoglucosenone with Ethyl Cyanoacetate under Michael Reaction Conditions

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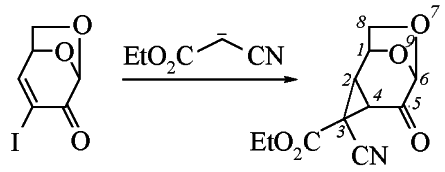
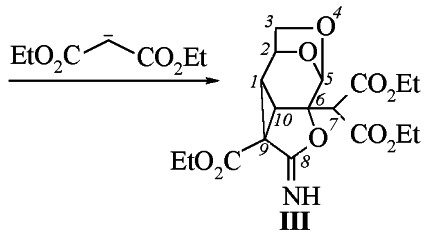
Abstract—The reaction of iodolevoglucosenone with the anion of ethyl cyanoacetate via succession of tandem intramolecular reactions leads to formation of tricyclic cyclopropanolevoglucosenone or tetracyclic imine.

Formerly in the course of investigation of reactions between iodolevoglucosenone (**I**) [1] and anions of CH-acids, in particular, with diethyl malonate and ethyl acetoacetate we observed formation of untrivial products, derivatives of cyclopropane [1, 2] and stable oxetanes [2, 3]. In the present study we carried out similar reactions of compound **I** with ethyl cyanoacetate.

Reaction between equimolar amounts of compound **I** and ethyl cyanoacetate sodium derivative was carried out in THF at –60°C. Under these conditions the reaction was fast and selective resulting in 80% yield in tricyclic [1+2]-adduct, cyclopropanolevoglucosenone (**II**). The reaction performed at 20°C gave rise to a new crystalline compound with an empirical formula corresponding to a levoglucosenone adduct with two molecules of ethyl cyanoacetate. The presence in the NMR spectra of double sets of closely located signals suggests the presence in the product of diastereomers mixture. It is presumable that in the first stage arises a cyclopropanolevoglucosenone **II** that further suffers attack of the second anion of ethyl cyanoacetate at the keto group resulting in further transformations. We checked this assumption by performing the reaction of compound **II** with ethyl cyanoacetate sodium derivative at 20°C. The reaction product was identical in composition and spectral characteristics to the previously obtained diastereomer mixture. At the same time compound **II** was treated with malonate-anion; the reaction afforded individual imine **III**.



I **II**



III

Compound **II** due to its diastereomeric homogeneity was easily identified. In its ^{1}H NMR spectrum the most characteristic resonances of the cyclopropane protons appear as doublets at 2.20 and 2.93 ppm with a coupling constant 8.7 Hz, and the singlet of the imine proton is observed at 5.84 ppm. In the ^{13}C NMR spectrum the signals from the same fragments are seen at 30.66, 31.78, and 36.98 ppm (cyclopropane ring), and 171.58 ppm (C=NH). Taking into account the spectral data of compound **III** we successfully assigned the signals in the spectra of diastereomer mixture of compound **IV** obtained in reaction of iodolevoglucosenone (**I**) with ethyl cyanoacetate sodium derivative at 20°C. In the ^{1}H NMR spectra the characteristic signals of cyclopropane protons appear as doublets with a coupling constant 8.6 Hz at 2.28 (2.34) and 2.83 (3.0) ppm, the singlet of imine proton at 6.29 (6.10) ppm. In the ^{13}C NMR spectra the signals of the cyclopropane ring carbons are observed at 30.51 (30.79), 37.59 (37.26) and 41.95 (41.46) ppm, those of imine carbon at 171.66 (171.78) ppm. The diastereomers obtained turned out to be relatively stable against acid hydrolysis (in 12% water solution of HCl). However in 10% KOH solution in THF–H_2O mixture (1 : 3) the ester group at

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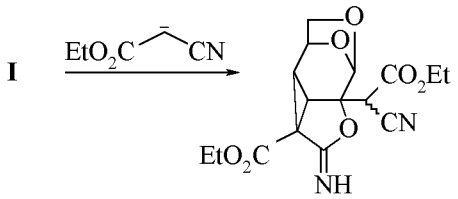
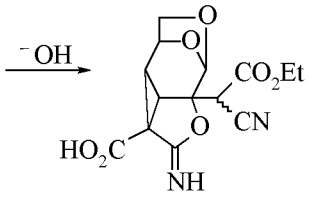
C^9 is readily hydrolyzed to give acid **V**. In the ^{13}C NMR spectra of the hydrolysis products this is evidenced by downfield shift of the α-carbons C^9 compared to $C^{1'}$ [4]. Whereas the resonances of C^9 in the spectra of diastereomers of compound **V** are observed at 42.30 (42.54) ppm, in compound **IV** these signals appear at 37.59 (37.26) ppm; the chemical shifts of $C^{1'}$ ar observed at 30.24 (30.85) and 30.89 (31.54) ppm respectively.



IV



V

We failed to obtain in a similar way lactone **VII** from bisethoxycarbonylcyclopropane derivative **VI**. Here arose the known [5] Michael adducts **VIII** diastereomeric with respect to $C^{1'}$ atom. The spectral characteristics thereof are identical to those of compound prepared by procedure [5].

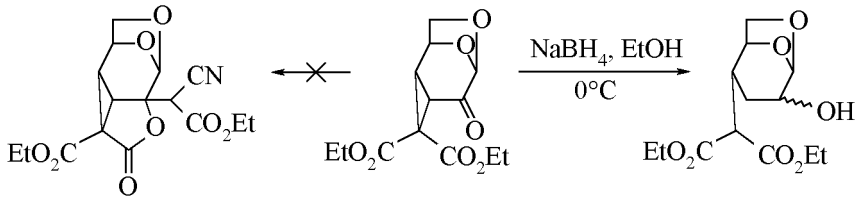
Presumably the cyclopropane compound **VI** is subjected to attack of ethyl cyanoacetate carbanion from the *endo*-region of bicyclo[5.1.$0^{2,4}$]octane on the most electron-deficient atom C^2 leading to the rupture of C^2–C^3 bond and malonate-anion elimination.

The stability of cyclopropane ring in compounds **II** and **VI** at hydrogenation depends significantly on electron-acceptor characteristics of substituents bonded to C^3 atom in agreement with the published data [6]. For instance, whereas the reduction with borohydride of compound **II** at 0°C occurs with no complications, this reaction with bisethoxtcarbonyl derivative of cyclopropane **VI** is accompanied by hydrogenolysis of the more strained bond C^3–C^4 and by formation of isomeric alcohols **IX** in 80% yield. The reaction carried out at –15°C furnished alongside the isomeric alcohols **IX** also only *exo*-alcohol **X** in 22% yield. The calculation of bond lengths performed by AM1 procedure [software Hyper Chem 5.01 (1996)] demonstrated that the bond C^3–C^4 in alcohols **X** and **XI** actually were the longest: 1.521 and 1.523 Å respectively.

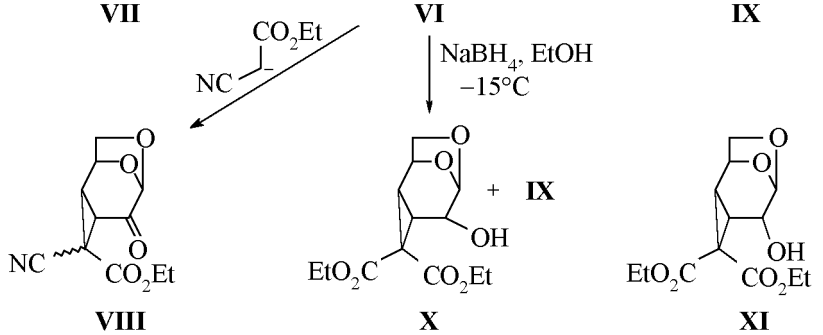
Thus iodolevoglucosenone in Michael reactions with ethyl cyanoacetate is prone to tandem transformations of anionotropic type.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were registered on spectrometer Bruker AM-300 at operating frequencies 300 and 75.47 MHz respectively from solutions in $CDCl_3$, internal reference TMS. TLC was performed on Silufol plates (Czechia). Optical rotation was measured on Perkin-Elmer-141 instrument. Mass spectra were registered on MKh-1306 device (ionizing voltage 70 eV, ionizing chamber temperature 30–50°C).



VII **VI** **IX**



VIII **X** **XI**

(1*R*,2*R*,3*R*,4*S*,6*R*)-5-Oxo-3-cyano-3-ethoxycarbonyl-7,9-dioxatricyclo[4.2.10^{2,4}]nonane (II). To a suspension of 0.08 g (3.4 mmol) of NaH in 3 ml of THF was added dropwise 0.24 ml (2 mmol) of ethyl cyanoacetate, and the mixture was stirred for 30 min. On cooling to –60°C 0.5 g (2 mmol) of iodolevoglucosenone in 2 ml of THF was added to the reaction mixture. After stirring for 15 min the temperature was raised to 0°C, the reaction mixture was acidified to pH 5 with 10% HCl solution, the reaction products were extracted into ethyl acetate (3×5 ml). The combined extracts were washed with saturated Na_2CO_3 solution, dried with Na_2SO_4, evaporated, and the residue was subjected to chromatography to afford 0.37 g (80%) of compound **II** as transparent crystals. R_f 0.43 (ethyl acetate–heptane, 9:1). mp 119–120°C. $[\alpha]_D^{16}$ –121.9° (*c* 1.0, $CHCl_3$). IR spectrum, cm^{-1}: 760, 930, 1000, 1110, 1130, 1150, 1250, 1320, 1390, 1660, 1700, 1750, 2280, 2890, 2920, 2990. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.29 t (3H, CH_3, 7.1), 2.38 d.d (1H, H^2, 8.4, 1.0), 2.63 d (1H, H^4, 8.4), 3.90 d.d (1H, H$^8_{exo}$, 7.5, 4.4), 4.11 d (H$^8_{endo}$, 7.5), 4.22 q (2H, OCH_2, 7.1), 4.98 d.d (1H, H^1, 4.4, 1.0), 5.0 s (1H, H^6). ^{13}C NMR spectrum, δ_C, ppm: 13.78 (CH_3), 22.10 (C^3), 28.31 (C^2), 32.42 (C^4), 64.01 (OCH_2), 68.64 (C^1), 69.64 (C^8), 99.02 (C^6), 113.48 (CN), 164.90 (CO), 189.08 (C^5). Found, %: C 55.5; H 4.6; N 5.9. $C_{11}H_{11}NO_5$. Calculated, %: C 55.7; H 4.6; N 5.9. Mass spectrum (electron impact), *m/z* (I_{rel}, %): 238 [*M*+H]$^+$ (1), 237 [*M*]$^+$ (3), 209 [*M*–CO]$^+$ (7), 192 (18), 191 (12), 181 (13), 178 (19), 163 (43), 149 (30), 134 (74), 123 (57), 121 (17), 106 (100).

(1*R*,2*S*,5*R*,6*S*,9*S*,10*S*)-6-[Bis(ethoxycarbonyl)-methyl-8-imino-9-ethoxycarbonyl-4,7,11-trioxa-tetracyclo[4.3.1.1^{2,5}.0^{9,10}]undecene (III). To a suspension of 0.06 g (2.5 mmol) of NaH in 2 ml of THF was added dropwise 0.27 ml (1.7 mmol) of diethyl malonate, and the mixture was stirred for 30 min. Then within 30 min was added a solution of 0.4 g (1.7 mmol) of compound **II** in 2 ml of THF. The reaction mixture was stirred for 20 min, treated with 3% water solution of HCl till pH 7, the reaction products were extracted into dichloromethane (3×5 ml). The combined extracts were washed with saturated aqueous NaCl solution, dried on $MgSO_4$, evaporated, and from the residue was isolated by chromatography 0.45 g (67%) of imine **III** as oily substance and 0.08 g of the initial compound **II**. **Compound III.** R_f 0.19 (ethyl acetate–heptane, 7:3). $[\alpha]_D^{25}$ +112.4° (*c* 1.0, $CHCl_3$). IR spectrum, cm^{-1}: 760, 880, 980, 1030, 1130, 1270, 1390, 1730, 2900, 2980. ^{1}H NMR spectrum, δ, ppm, (*J*, Hz): 1.25 m (9H, 3CH_3), 2.20 d (1H, H^1, 8.7), 2.93 d (1H, H^{10}, 8.7), 3.72 s (1H, H$^{1'}$), 3.95 d.d (1H, H$^3_{exo}$, 7.0, 3.8), 4.07 d (1H, H$^3_{endo}$, 7.0), 4.22 m (6H, 3OCH_2), 4.88 br.s (1H, H^2), 5.38 s (1H, H^5), 5.84 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 13.89, 13.95, 14.04 (3CH_3), 30.66 (C^1), 31.78 (C^{10}), 36.98 (C^9), 54.34 (C$^{1'}$), 58.06 (C^3), 62.02, 62.17, 62.25 (3OCH_2), 70.74 (C^2), 73.72 (C^6), 100.87 (C^5), 166.18, 166.44, 167.74 (CO_2), 171.58 (C=NH). Mass spectrum (electron impact), *m/z* (I_{rel}, %): 397 [*M*]$^+$ (1.5), 396 [*M*–H]$^+$ (3), 369 [*M*–C_2H_4]$^+$ (1), 352 [*M*–OEt]$^+$ (24), 351 [*M*–EtOH]$^+$ (43), 324 [*M*–CO_2Et]$^+$ (52), 309 (19), 305 (10), 234 (14), 232 (10), 279 (38), 206 (100), 178 (14), 160 (81), 134 (19), 132 (12), 106 (6), 104 (8).

(1*R*,2*S*,5*R*,6*S*,9*S*,10*S*)-8-Imino-6-[(1*RS*)-1-cyano-1-ethoxycarbonylmethyl]-9-ethoxycarbonyl-4,7,11-trioxatetracyclo-[4.3.1.1^{2,5}.0^{9,10}]undecane (IV). (a) To a suspension of 0.14 g (6 mmol) of NaH in 3 ml of THF was added dropwise 0.52 g (4 mmol) of ethyl cyanoacetate, and the mixture was stirred for 30 min. Then to the reaction mixture was added a solution of 0.5 g (2 mmol) of iodolevoglucosenone in 2 ml of THF. After stirring the mixture for 15 min it was acidified with 10% water solution of HCl till pH 5, the reaction products were extracted into ethyl acetate (3×5 ml). The combined extracts were washed with saturated Na_2CO_3 solution, dried with Na_2SO_4, evaporated, and the residue was subjected to chromatography to afford 0.5 g (72%) of compound **IV** as transparent crystals.

(b) To a suspension of 0.06 g (2.5 mmol) of NaH in 2 ml of THF was added dropwise 0.22 g (1.7 mmol) of ethyl cyanoacetate, and the mixture was stirred for 30 min. Then to the reaction mixture was added a solution of 0.4 g (1.7 mmol) of compound **II** in 2 ml of THF. The reaction mixture was stirred for 30 min and then treated with 10% water solution of HCl till pH 7, the reaction products were extracted into dichloromethane (3×5 ml). The combined extracts were washed with saturated aqueous NaCl solution, dried on $MgSO_4$, evaporated, and from the residue was isolated by chromatography 0.47 g (80%) of imine **IV**. R_f 0.24 (ethyl acetate–heptane, 9:1), mp 115–116°C (ethyl acetate). $[\alpha]_D^{10}$ +50.7° (*c* 1.0, $CHCl_3$). IR spectrum, cm^{-1}: 780, 1100, 1330, 1370, 1460, 1640, 1710, 2850, 2880, 2920. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.32 t (3H, 2CH_3, 7.0), 1.38 t (3H, 2CH_3, 7.0), 2.34 d (1H, H^1, 8.6) and 2.28 d (1H, H^1, 8.6), 2.83 d (1H, H^{10}, 8.6) and 3.0 d (1H, H^{10}, 8.6), 4.06 s (1H, H$^{1'}$) and 4.03 (1H, H$^{1'}$), 4.22 m (2H, 4OCH_2), 4.32 m (2H, 2H$_3$), 5.0 br.s (1H, 2H^2), 5.32 s (1H, H^5) and 5.39 s (1H,

H^5), 6.29 s (1H, NH) and 6.10 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 13.83 (CH_3), 13.92 ($3CH_3$), 30.51 and 30.79 (C^{1}), 30.89 and 31.54 ($C^{1'}$), 37.59 and 37.26 (C^{9}), 41.95 and 41.46 (C^{10}), 62.25, 63.67, 62.33 and 63.93 (OCH_2), 70.77 and 70.56 (C^{2}), 73.91 and 73.87 (C^{6}), 100.21 and 100.77 (C^{5}), 113.26 and 113.14 (CN), 162.91 and 163.05 (CO_2Et), 167.15 ($2CO_2Et$), 171.66 and 171.78 (C=NH). Found, %: C 54.1; H 5.1; N 6.9. $C_{16}H_{18}N_2O_7$. Calculated, %: C 54.8; H 5.1; N 8.0. Mass spectrum (electron impact), *m/z* (I_{rel}, %): 350 $[M]^+$ (3), 305 $[M–OEt]^+$ (10), 277 $[M–CO_2Et]^+$ (9), 252 (5), 232 (43), 231 (13), 206 (8), 205 (10), 192 (5), 187 (6), 186 (7), 177 (8), 160 (46), 159 (100), 147 (17), 116 (37), 85 (74).

(1*R*,2*S*,5*R*,6*S*,9*S*,10*S*)-8-Imino-6-[(1*RS*)-1-cyano-1-ethoxycarbonylmethyl]-4,7,11-trioxatetracyclo[4.3.1.1^{2,5}.0^{9,10}]-undecan-9-oic acid (V). A solution of 0.2 g (0.57 mmol) of compound **IV** in 3 ml of THF was cooled to 0°C, and 1 ml of 30% water solution of KOH was added. After stirring for 15 min the mixture was acidified with 2 ml of 10% water solution of HCl. Acid V was extracted by ethyl acetate (3 × 5 ml). The combined organic extracts were dried with $MgSO_4$ and evaporated. We obtained 0.09 g (50%) of colorless crystals of compound **V**. R_f 0.22 (ethyl acetate–hexane, 9 : 1). mp 107–108°C (ethyl ether). $[\alpha]_D^{25}$ +76.3° (*c* 1.0, CH_3OH). IR spectrum, cm^{-1}: 800, 900, 930, 1050, 1150, 1330, 1380, 1470, 1710, 1750, 2860, 2970, 3280. ^1H NMR spectrum (CD_3OD), δ, ppm (*J*, Hz): 1.23 t (6H, $2CH_3$, 7.0), 2.24 d (1H, H^{1}, 8.8) and 2.26 d (1H, H^{1}, 8.8), 2.65 d (1H, H^{10}, 8.8) and 2.79 d (1H, H^{10}, 8.8), 3.85 br.s (2H, $2H^{1'}$), 4.18 d (2H, H^{3}_{endo}, 11.0), 4.20 q (2H, CH_2O, 7.0) and 4.30 q (2H, CH_2O, 7.0), 4.48 d (2H, H^{3}_{exo}, 11.0), 5.0 br.s (2H, H^{2}), 5.15 s (1H, H^{5}) and 5.26 s (1H, H^{5}), 7.64 s (1H, NH) and 7.52 s (1H, NH), 12.98 br.s (2H, CO_2H). ^{13}C NMR spectrum (CD_3OD), δ_C, ppm: 13.50 ($2CH_3$), 29.61 and 29.43 (C^{1}), 30.24 and 30.85 ($C^{1'}$), 37.40 ($2C^{10}$), 42.30 and 42.54 (C^{9}), 58.05 ($2C^{3}$), 62.69 and 62.59 (CH_2O), 70.0 and 70.30 (C^{2}), 73.33 ($2C^{6}$), 100.51 and 99.82 (C^{5}), 114.29 and 114.55 (CN), 163.19 and 162.93 (CO_2H), 168.47 ($2CO_2Et$), 171.81 and 171.33 (C=NH).

(1*R*,4*R*,5*R*)-4-[(1*RS*)-1-Cyano-1-ethoxycarbonylmethyl]-7,8-dioxabicyclo[3.2.1]octan-2-one (VIII). To a suspension of 0.04 g (1.54 mmol) of NaH in 2 ml of THF was added dropwise 0.1 g (0.77 mmol) of ethyl cyanoacetate, and the mixture was stirred for 30 min. Then to the reaction mixture was added a solution of 0.22 g (0.77 mmol) of compound **VI** in 2 ml of THF. The reaction mixture was stirred for 30 min and then treated with 10% water solution of HCl till pH 5, the reaction products were extracted into dichloromethane (3 × 5 ml). The combined extracts were washed with saturated aqueous NaCl solution, dried on $MgSO_4$, evaporated, and from the residue by chromatography was separated an oily isomers mixture of compound **VIII**. R_f 0.38 (ethyl acetate–heptane, 7 : 3). IR spectrum, cm^{-1}: 880, 930, 1000-1140, 1220, 1280, 1390, 1430, 1460, 1640, 1750, 2280, 2940, 3000. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.34 t (3H, CH_3, 7.2) and 1.36 t (3H, CH_3, 7.1), 2.32 d.d (1H, H^{3a}, 2.2, 17.0) and 2.62 d.d (1H, H^{3a}, 1.6, 16.8), 2.82 m (2H, $2H^{3e}$), 2.90 d.d.d.d (1H, H^{4}, 1.6, 2.2, 3.7, 9.7) and 2.95 d.d.d.d (1H, H^{4}, 1.2, 1.6, 3.1, 8.0), 3.70 d (1H, H^{5}, 9.7) and 3.81 d (1H, H^{5}, 8.0), 4.05 d (1H, H^{6}_{endo}, 9.5) and 4.07 d (1H, H^{6}_{endo}, 8.9), 4.08 d (1H, H^{6}_{exo}, 9.5) and 4.12 d (1H, H^{6}_{exo}, 8.9), 4.27 q (2H, CH_2O, 7.2) and 4.29 q (2H, CH_2O, 7.1), 4.75 br.s (1H, $C^{1'}H$) and 4.91 br.s (1H, $C^{1'}H$), 5.14 s (1H, H^{1}) and 5.16 s (1H, H^{1}). ^{13}C NMR spectrum, δ_C, ppm: 13.95 and 13.90 (CH_3), 34.43 and 34.72 (C^{3}), 41.05 ($2C^{4}$), 39.70 and 40.01 ($C^{1'}$), 63.65 ($2OCH_2$), 67.68 and 67.79 (C^{6}), 73.92 and 74.23 (C^{5}), 101.47 and 101.56 (C^{1}), 114.87 and 115.19 (CN), 164.56 and 164.70 (CO_2), 196.41 and 196.81 (C^{2}). Mass spectrum (electron impact), *m/z* (I_{rel}, %): 239 $[M]^+$ (2), 212 (5), 211 (23), 194 (15), 193 (9), 185 (6), 171 (16), 167 (7), 166 (6), 160 (12), 138 (23), 133 (6), 125 (8), 115 (10), 99 (100), 71 (82), 43 (94).

(1*R*,2*RS*,4*R*,5*R*)-4-[Bis(ethoxycarbonyl)-methyl]-7,8-dioxabicyclo[3.2.1]octan-2-ol (IX). To a solution of 0.45 g (1.58 mmol) of acid **V** in 6 ml of anhydrous ethanol cooled to 0°C was added 0.12 g (3.6 mmol) of $NaBH_4$. After stirring for 1 h the reaction mixture was neutralized with concn. CH_3COOH, evaporated, the residue was diluted with water, and the reaction products were extracted into dichloromethane (3×5 ml). The combined extracts were dried on $MgSO_4$, evaporated, and the residue was subjected to chromatography to afford 0.36 g (80%) of oily mixture of compound **IX** isomers. IR spectrum, cm^{-1}: 860, 900, 980–1340, 1380, 1460, 1730, 2900, 2920, 2970, 3460. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.27 m ($4CH_3$), 1.48 d.d (1H, H^{3a}, 15.4, 1.0) and 2.10 m (1H, H^{3a}, 15.4), 1.60–1.75 m (2H, H^{3e}), 2.28 m (1H, H^{4}) and 2.42 m (1H, H^{4}), 3.55 br.s (1H, H^{2}) and 3.64 d.d (1H, H^{2}, 6.1, 10.2), 3.70 d (2H, $H^{1'}$, 11.5), 3.80–3.90 m (4H, H^{6}), 4.17 m (8H, OCH_2), 4.43 br.s (2H, H^{5}), 5.28 s (1H, H^{1}) and 5.30 s (1H, H^{1}). ^{13}C NMR spectrum, δ_C, ppm: 13.88 ($4CH_3$), 25.74 and 28.36 (C^{3}), 35.68 and 37.87 (C^{4}), 52.73 and 53.81 ($C^{1'}$), 61.58 ($4OCH_2$), 66.06 and 66.18

(C^2), 67.28 and 68.46 (C^6), 73.89 and 74.12 (C^5), 102.40 and 103.0 (C^1), 168.17, 168.28 and 168.60, 169.03 (4CO). From the mixture obtained by repeated chromatography was isolated as individual substance the more polar **2*S*-isomer.** R_f 0.28 (ethyl acetate–hexane, 9:1). $[\alpha]_D^{25}$ −53.7° (*c* 1.0, $CHCl_3$). IR spectrum, cm^{-1}: 880, 920, 1000, 1070, 1160, 1210, 1280, 1320, 1390, 1460, 1730, 2880, 3450. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.15 t and 1.17 t (6H, CH_3, 7.1), 1.62 d.d.d (1H, H^3, 6.3, 8.0, 10.2), 1.68 d.d (1H, H^3, 6.3, 8.0), 2.20 br.s (1H, OH), 2.38 d.d (1H, H^4, 6.1, 11.3), 3.60 d.d (1H, H^2, 6.3, 10.2), 3.65 d (1H, $H^{1'}$, 11.3), 3.78 d.d (1H, H^6_{exo}, 3.4, 7.6), 3.83 d.d (1H, H^6_{endo}, 1.0, 7.6), 4.11 q and 4.14 q (4H, OCH_2, 7.1), 4.38 d.d (1H, H^5, 1.0, 3.4), 5.22 s (1H, H^1). ^{13}C NMR spectrum, δ_C, ppm: 13.95 ($2CH_3$), 28.46 (C^3), 37.93 (C^4), 52.77 ($C^{1'}$), 61.63 ($2OCH_2$), 66.24 (C^2), 68.52 (C^6), 73.94 (C^5), 103.01 (C^1), 168.20 and 168.34 (CO).

(1*R*,2*R*,4*S*,5*S*,6*R*)-3-(Bisethoxycarbonyl)-5-hydroxy-7,9-dioxatricyclo[4.2.1.$0^{2,4}$]nonane (X). The reaction carried out along the above procedure at −15°C gave rise to compounds **IX** and **X** obtained in 77 and 22% yield respectively. Alcohol **X**. R_f 0.39 (ethyl acetate– hexane, 9:1). $[\alpha]_D^{25}$ −54.7° (*c* 1.0, $CHCl_3$). IR spectrum, cm^{-1}: 940, 1060, 1090, 1220, 1270, 1340, 1390, 1730, 2920, 3000, 3430. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.22 t (3H, CH_3, 7.0), 1.30 t (3H, CH_3, 7.0), 1.88 d (1H, H^2, 9.1), 2.18 d.d (1H, H^4, 8.0, 9.1), 3.65 d.d (1H, H^8_{exo}, 4.4, 7.0), 3.82 d.d (1H, H^5, 8.0, 11.9), 3.88 d (1H, H^8_{endo}, 7.0), 4.14 q (2H, OCH_2, 7.0), 4.28 q (2H, OCH_2, 7.0), 4.68 d (1H, H^9, 4.4), 5.15 s (1H, H^6), 5.18 d (1H, OH, 11.9). ^{13}C NMR spectrum, δ_C, ppm: 13.84, 13.91 ($2CH_3$), 25.61 (C^2), 27.12 (C^4), 35.81 (C^3), 62.23, 62.46 ($2OCH_2$), 67.51 (C^8), 67.63 (C^5), 68.92 (C^1), 103.98 (C^6), 169.35 ($2CO_2$).

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