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Stereoselective Synthesis of New (+)-1-{(1*R*,3*R*,6*S*)-4,7,7-Trimethylbicyclo[4.1.0]hept-4-en-3-yl}ethan-1-one Derivatives

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Abstract—A procedure was developed for the stereoselective synthesis of aminated derivatives of (+)-1-{(1*R*,3*R*,6*S*)-4,7,7-trimethylbicyclo[4.1.0]hept-4-en-3-yl}ethan-1-one. The configuration of the side-chain chiral center in (+)-1-{(1*R*,3*R*,6*S*)-4,7,7-trimethylbicyclo[4.1.0]hept-4-en-3-yl}ethan-1-ol was determined by X-ray analysis. Diketene and Meldrum's acid were proposed as initial compounds for the synthesis of, respectively, 3-oxobutanoic and malonic acid esters having a 1-ethyl-4,7,7-trimethylbicyclo[4.1.0]hept-4-ene fragment.

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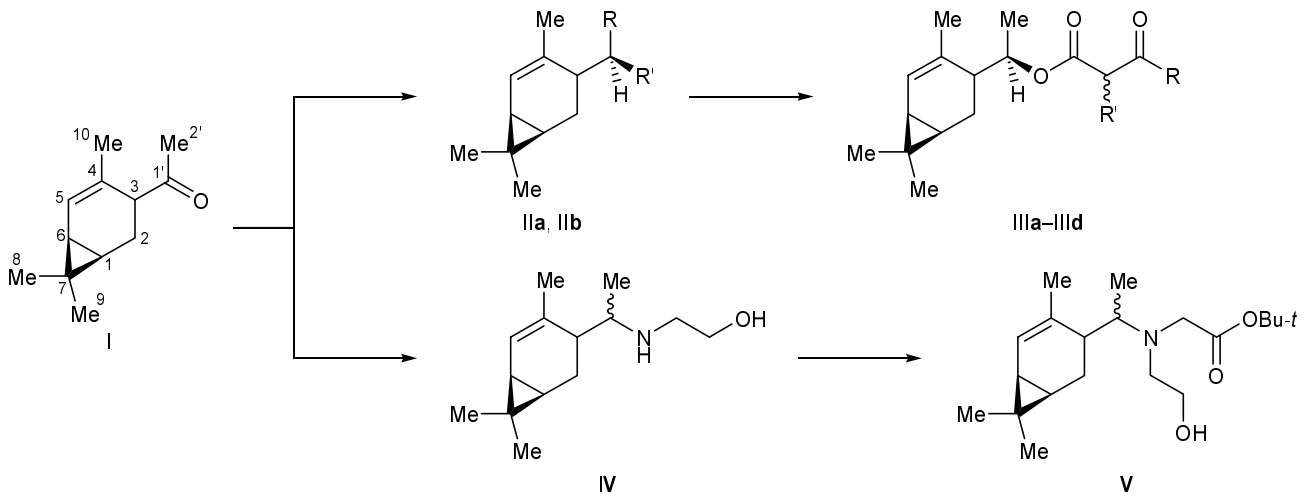
(+)-1-{(1*R*,3*R*,6*S*)-4,7,7-Trimethylbicyclo[4.1.0]-hept-4-en-3-yl}ethan-1-one (**I**) contains a dimethylcyclopropane fragment typical of a number of target compounds; it is accessible on a large scale with a high optical purity and is the subject of persistent researchers' interest [1]. (+)-4α-Acetyl-2-carene (**I**) reduction products have recently been proposed as intermediate compounds in the synthesis of chiral blocks for building up carbon analogs of epothilons [2]. Two versions of synthesis of stereoisomeric alcohols **IIa** and **IIb** from compound **I** have been reported: (1) via hydrogenation over nickel catalyst [3] and (2) by reduction with sodium tetrahydridoborate [2, 4]. However, the configuration of the newly formed asymmetric center was not determined, and stereoisomers **IIa** and **IIb** were not separated [2, 4]. This aspect is important, especially for carbon analogs of compounds characterized by a taxol-like mechanism of action [5].

Scheme 1.



II, R = Me, R' = OH (**a**); R = OH, R' = Me (**b**); **III**, R = Me (**a**, **b**), CH_2Cl (**c**), OH (**d**); R' = H (**a**, **c**, **d**), Cl (**b**).

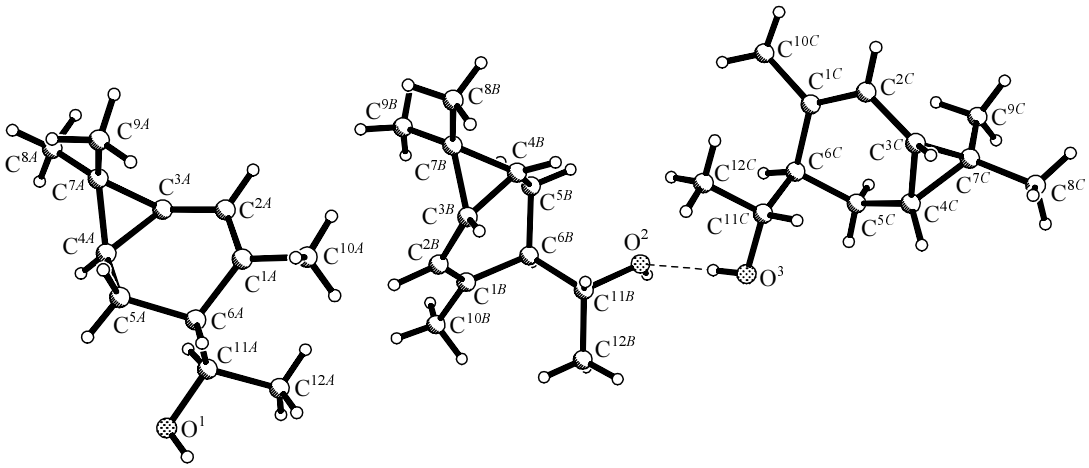


Fig. 1. Homomolecular structure of alcohol **IIa** in crystal.

In the present work we reduced ketone **I** with sodium tetrahydridoborate and obtained compound **II** as a crystalline substance with the same melting point as that reported in [3] for the hydrogenation product of **I**. Nevertheless, the configuration of the side-chain chiral center (C^1) in the resulting alcohol remained unclear (Scheme 1). Therefore, compound **II** was examined by the X-ray diffraction method. X-Ray analysis of **II** was also performed previously by Puranik et al. [6]; however, there were no data on the synthesis of this compound, and the configuration of C^6 assigned in [2, 6] was doubtful. Taking into account that the seniority of the substituents on C^6 decreases counterclockwise, the C^6 chiral center should be denoted as *S* rather than *R*.

The first version of structure solution was analogous to that given in [6]; it was characterized by fairly good R_1 and GooF parameters (0.057 and 1.034, respectively). However, the calculated Flack parameter *x* [7] was equal to 1.482, indicating invalid identification

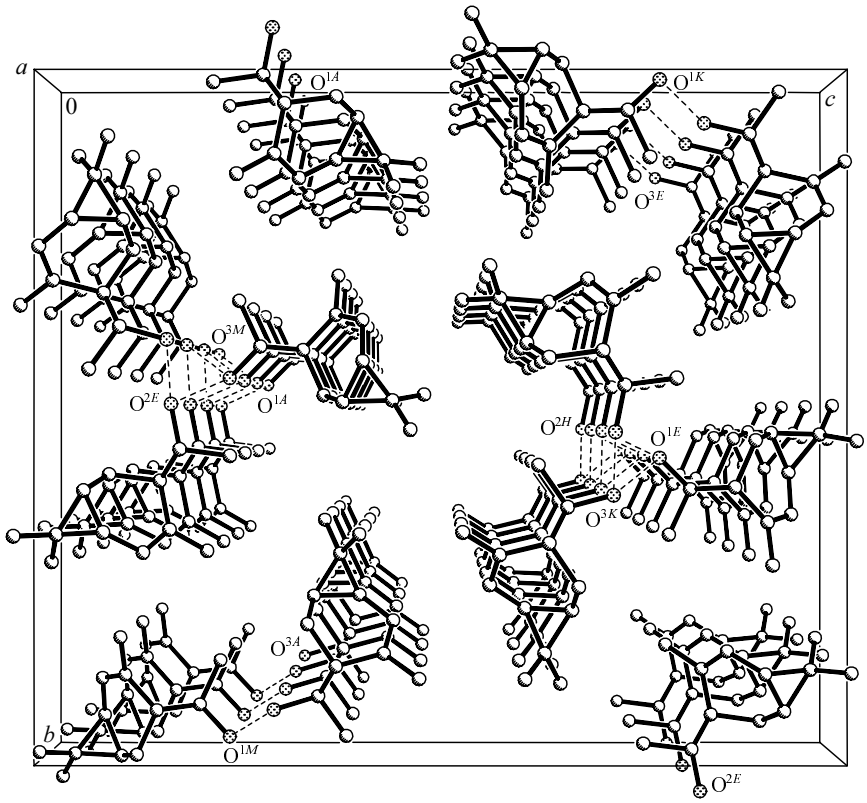


Fig. 2. A fragment of helical chains in the crystalline structure of alcohol **IIa** along the *100* axis. Hydrogen atoms are not shown.

of the absolute configuration of **II**. This means that the corresponding enantiomer was examined in [6]. Using the inversion operation and repeated structure refinement we obtained the absolute configuration corresponding to stereoisomer **IIa** with the following final parameters: $R_1 = 0.057$, GooF = $S = 1.020$.

The crystal structure of compound **II** is homomolecular; an independent part of a unit cell contains three crystallographically independent molecules (*A*, *B*, and *C*) having the same composition ($C_{12}H_{20}O$) and structure (Fig. 1). Molecules *B* and *C* are turned apart in such a way that a strong intermolecular hydrogen bond is formed between these molecules, O^3–$H^3\cdots O^2$ 2.659(2) Å. The C^{11} atom deviates from the $C^6C^{12}O$ plane by 0.449(3), 0.451(3), and –0.447(3) Å for molecules *A*, *B*, and *C*, respectively; the H^{11} atom deviates from the same plane by 1.459(3), 1.441(3), and –1.457(3) Å, respectively. The H^6 and H^{11} atoms are arranged *trans*, and the torsion angle $H^{11}C^{11}C^6H^6$ is 163.6 (*A*), 175.4 (*B*), and 172.7° (*C*), indicating *R* configuration of the C^{11} side-chain chiral center.

Molecules of **IIa** in crystal give rise to a two-dimensional pattern via intermolecular hydrogen bonding along double screw axes, $O^1H^1\cdots O^3$ [2.664(5) Å; $-x + 3$, $y - 1/2$, $-z + 3/2$] and $O^2H^2\cdots O^1$ [2.659(5) Å; $-x + 2$, $y + 1/2$, $-z + 3/2$]. As a result, infinite helical chains are formed (Fig. 2).

We also found that *R* isomer **IIa** can readily be separated from *S* isomer **IIb** by crystallization from hexane. The reduction of ketone **I** with sodium tetrahydridoborate in aqueous dioxane gives 85% of epimer mixture **IIa**/**IIb** (3:2, according to the ^{1}H NMR data). Replacement of aqueous dioxane by methanol and reduction of the temperature to –15°C does not decrease the overall yield of diastereoisomers **IIa** and **IIb** but increases the fraction of epimer **IIa** to 60%.

Esters derived from carboxylic acids having an activated α-methylene group, such as 3-oxobutanoic or malonic acid, are widely used in the synthesis of heteroatom compounds [8–11], including chiral ones [12–14]. In order to obtain chiral compounds in an optically active form, it is advisable to use enantiomerically pure precursors [15]. Carboxylic acid esters can be synthesized by both direct and indirect methods. We obtained ester **IIIa** in 51% yield by transesterification of ethyl acetoacetate with alcohol **IIa**. We succeeded in raising the yield of **IIIa** to 98% by condensation of alcohol **IIa** with diketene in the presence of triethylamine. The ^{1}H NMR spectrum of **IIIa** characteristically contained five three-proton signals from methyl groups: four singlets at δ 0.79, 0.98, 1.65, and 2.22 ppm and a doublet as δ 1.17 ppm. One two-proton singlet from the methylene group of the 3-oxobutanoate fragment (δ 3.39 ppm) and two one-proton multiplets at δ 4.90–5.38 (CHO) and 5.40–5.5 ppm (CH=) were also present.

α-Halo ketones, including 2- and 4-chloroacetoacetic acid esters, are convenient intermediate products in the synthesis of functionalized heterocyclic compounds [16–18]. By reaction of ethyl 2-chloroacetoacetate with alcohol **IIa** under the same conditions as in the synthesis of ester **IIIa** we obtained a mixture of stereoisomeric esters **IIIb**. Unlike compound **IIIa**, in the ^{1}H NMR spectrum of **IIIb** we observed a double set of signals with an intensity ratio of 5:4 due to the presence of an additional chiral center (C^2) in the initial ester molecule. Taking into account that this center is not involved in the transesterification process, pure epimers of **IIIb** could be obtained from enantiopure ethyl 2-chloroacetoacetate. By analogous reaction with ethyl 4-chloroacetoacetate we synthesized α-chloro ketone **IIIc**. Its ^{1}H NMR spectrum lacked three-proton singlet at δ 2.22 ppm but contained a two-proton signal at δ 4.16 ppm due to the CH_2Cl group. Alcohol **IIa** was also brought into reaction with 2,2-dimethyl-1,3-dioxane-4,6-dione, which led to malonic acid monoester **IIId**. The structure of compound **IIId** was confirmed by the analytical data and IR and ^{1}H NMR spectra.

Nitrogen-containing compounds and amino derivatives of natural compounds constitute a large part of substances possessing practically important properties [19–21]. For example, enantiomerically pure antitubercular drug (+)-Ethambutol contains a (2*R*)-1-oxomethyl-2-aminopropyl fragment [22]. A mild and convenient method for the introduction of that fragment into the (+)-4α-acetyl-2-carene (**I**) molecule was treatment of the latter with 2-aminoethanol in the presence of $NaBH_3CN$. Compound **IV** thus obtained was a mixture of epimers at the side-chain C^1 atom (9:1, according to the ^{1}H NMR data). Alkylation of **IV** at the nitrogen atom with *tert*-butyl bromoacetate gave N-substituted aminoacetic acid ester **V** (Scheme 1).

We can conclude that the reduction of accessible (+)-4α-acetyl-2-carene (**I**) with sodium tetrahydridoborate occurs in a stereoselective fashion to give (+)-(1*R*)-1-{(1*R*,3*R*,6*S*)-4,7,7-trimethylbicyclo[4.1.0]-hept-4-en-3-yl}ethan-1-ol (**IIa**) as the major stereoisomer; transesterification of ethyl acetoacetate or its 2- and 4-chloro derivatives with alcohol **IIa** gives the

corresponding esters **IIIa**–**IIId**. The aminoalkylation–alkylation sequence is convenient for the synthesis of aminated derivatives of compound **I**.

EXPERIMENTAL

The specific rotations were measured on Perkin–Elmer 141 and Perkin–Elmer 241 polarimeters in $CHCl_3$. The IR spectra were recorded on Specord 74-1 and FT-IR Biorad FTS 7 instruments from solutions in carbon tetrachloride. The melting points were determined on a Boetius melting point apparatus and are uncorrected. The ^1H and ^{13}C NMR spectra were obtained on Bruker AC-E 200 and Bruker AC-80 spectrometers from solutions in $CDCl_3$; the chemical shifts were referenced to tetramethylsilane (internal standard). Silica gel L 40/100, 100/160 (Czechia), and 40/63 μm (Fluka) was used for column chromatography. Thin-layer chromatography was performed on Silufol and Alufol plates (Czechia); spots were visualized by treatment with a 5% solution of phosphotungstic acid in ethanol, followed by heating, or with an acid 2% aqueous solution of $KMnO_4$. The solvents and reagents used were purified by the procedure described in [23]. Solutions in organic solvents were dried with anhydrous sodium or magnesium sulfate.

X-Ray diffraction study of a single crystal of compound IIa. A set of experimental reflections was acquired on a Bruker Nonius diffractometer; 6091 independent reflections with $I > 4\sigma(I)$ were used in the structure solution and refinement. The structure was solved and refined using SHELXS97 and SHELXL97 software [24]. Rhombic crystals belonging to space group $P2_12_12_1$ with the following unit cell parameters: a = 5.7909(1), b = 22.3462(6), c = 26.0770(8) Å; d_{calc} = 1.065 g/cm^3; Z = 12; $C_{12}H_{20}O_1$. Hydrogen atoms were localized by the Fourier difference synthesis; the positions of non-hydrogen and hydrogen atoms were refined, respectively, in anisotropic and isotropic approximations.

(+)-1-{(1*R*,3*R*,6*S*)-4,7,7-Trimethylbicyclo[4.1.0]-hept-4-en-3-yl}ethan-1-one (I) was synthesized by the procedure described in [25], n_D^{20} = 4869, $[\alpha]_D^{20}$ = +365.5° (d = 1, neat).

(+)-(1*R*)-1-{(1*R*,3*R*,6*S*)-4,7,7-Trimethylbicyclo-[4.1.0]hept-4-en-3-yl}ethan-1-ol (IIa). *a*. A solution of 2 g (1.1 mmol) of ketone **I** in 10 ml of methanol was cooled to –15°C, 0.42 g (1.1 mmol) of $NaBH_4$ was added in portions, and the mixture was kept for 48 h at that temperature. Ammonium chloride, 1.5 g, and a saturated aqueous solution of ammonium chloride, 5 ml, were added in succession, and the mixture was extracted with hexane (3 × 50 ml). After appropriate treatment, removal of the solvent from the extract left 1.6 g of an oily material which crystallized from a solution in hexane. Amorphous substance, mp 51–54°C, $[\alpha]_D^{20}$ = +211.9° (c = 0.39, $CHCl_3$). Recrystallization from 3 ml of hexane gave 1.21 g (60%) of compound **IIa** as colorless crystals with mp 82–83°C; published data [3]: mp 82°C; $[\alpha]_D^{20}$ = +153.2° (c = 0.2, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3630, 1550, 1385, 1253, 1005. ^1H NMR spectrum, δ, ppm: 0.77–0.93 m and 1.15–1.23 m (2H, 1-H, 6-H), 0.84 s and 1.02 s (6H, C^8H_3, C^9H_3), 1.20 d (3H, $C^{2'}H_3$, J = 6.0 Hz), 1.35–1.48 m and 1.61–1.73 m (2H, 2-H), 1.74 s (3H, $C^{10}H_3$), 2.09–2.35 m (2H, 3-H, OH), 3.92 d.q (1H, 1'-H, J = 8.31, 6.21 Hz), 5.52–5.60 m (1H, 5-H). ^{13}C NMR spectrum, δ_C, ppm: 137.56 (C^4), 122.56 (C^5), 69.11 ($C^{1'}$), 45.35 (C^3), 27.67 (C^1), 24.33 (C^7), 23.59 (C^2), 21.37 (C^8), 20.78 (C^{10}), 20.06 ($C^{2'}$), 18.56 (C^6), 14.95 (C^9). Found, %: C 80.12; H 11.06. $C_{12}H_{20}O$. Calculated, %: C 79.94; H 11.18.

b. Sodium tetrahydridoborate, 0.5 g, was added in portions under vigorous stirring to a mixture of 1.78 g (1 mmol) of ketone **I** and 12 ml of 20% aqueous 1,4-dioxane. The mixture was stirred overnight, poured into 50 ml of water, neutralized with 10% hydrochloric acid to pH 7, and extracted with hexane (4 × 50 ml). After appropriate treatment, we isolated 1.53 g (85%) of an oily material which was a mixture of epimers **IIa** and **IIb** at a ratio of 3 : 2 (^1H NMR data).

(1*R*)-1-{(1*R*,3*R*,6*S*)-4,7,7-Trimethylbicyclo[4.1.0]-hept-4-en-3-yl}ethyl 3-oxobutanoate (IIIa). *a*. A mixture of 1 g (0.55 mmol) of alcohol **IIa**, 0.72 g (0.055 mmol) of ethyl acetoacetate, and 0.2 g of 4-dimethylaminopyridine in 6 ml of toluene was heated for 72 h under reflux. The solvent was distilled off, and the residue was subjected to column chromatography on 18 g of silica gel using hexane–diethyl ether (4:1) as eluent. Yield 0.75 g (51%). Pale yellow oily substance, bp 135–140°C (13 mm). IR spectrum, ν, cm^{-1}: 1735, 1720, 1670, 1375. ^1H NMR spectrum, δ, ppm: 0.74–0.90 m and 1.15–1.25 m (2H, 1-H, 6-H), 0.79 s and 0.98 s (6H, C^8H_3, C^9H_3), 1.17 d (3H, $C^{2'}H_3$, J = 6.44 Hz), 1.31–1.48 m and 1.61–2.13 m (2H, 2-H), 1.65 s (3H, $C^{10}H_3$), 2.0–2.39 m (1H, 3-H), 2.22 s (3H, COMe), 3.39 s (2H, $COCH_2$), 4.90–5.38 m (1H, 1'-H), 5.40–5.5 m (1H, 5-H). Found, %: C 72.76; H 9.1. $C_{16}H_{24}O_3$. Calculated, %: C 72.69; H 9.15.

b. Three drops of triethylamine were added to a mixture of 2 g (0.011 mmol) of alcohol **IIa** and 1.1 g

(0.013 mmol) of diketene in 10 ml of anhydrous benzene, and the mixture was stirred for 24 h at room temperature. After appropriate treatment, followed by chromatographic purification, we isolated 2.82 g (98%) of compound **IIIa** which was identical to a sample obtained as described above in *a*.

(1*R*)-1-{(1*R*,3*R*,6*S*)-4,7,7-Trimethylbicyclo[4.1.0]-hept-4-en-3-yl}ethyl 2-chloro-3-oxobutanoate (IIIb) was synthesized as described above for compound **IIIa** according to method *a*. Yield 40%, yellow substance. IR spectrum, ν, cm^{-1}: 1740, 1710. ^1H NMR spectrum, δ, ppm (major stereoisomer): 0.70–0.92 m and 1.13–1.20 m (2H, 1-H, 6-H), 0.77 s and 0.96 s (6H, C^8H_3, C^9H_3), 1.17 d (3H, $C^{2'}H_3$, J = 6.40 Hz), 1.29–1.41 m and 1.61–1.99 m (2H, 2-H), 1.63 s (3H, $C^{10}H_3$), 2.0–2.37 m (1H, 3-H), 2.35 s (3H, COMe), 4.68 s (1H, CHCl), 4.93–5.31 m (1H, 1'-H), 5.38–5.5 m (1H, 5-H). Found, %: C 64.21; H 7.58. $C_{16}H_{23}ClO_3$. Calculated, %: C 64.31; H 7.76.

(1*R*)-1-{(1*R*,3*R*,6*S*)-4,7,7-Trimethylbicyclo[4.1.0]-hept-4-en-3-yl}ethyl 4-chloro-3-oxobutanoate (IIIc) was synthesized as described above for compound **IIIa** according to method *a*. Yield 43%, yellow oily substance. IR spectrum, ν, cm^{-1}: 1710, 1700. ^1H NMR spectrum, δ, ppm: 0.71–0.92 m and 1.10–1.24 m (2H, 1-H, 6-H), 0.78 s and 0.97 s (6H, C^8H_3, C^9H_3), 1.17 d (3H, $C^{2'}H_3$, J = 6.4 Hz), 1.30–1.40 m and 1.60–1.96 m (2H, 2-H), 1.63 s (3H, $C^{10}H_3$), 2.0–2.37 m (1H, 3-H), 3.57 s (2H, $COCH_2CO$), 4.16 s (2H, CH_2Cl), 4.95–5.28 m (1H, 1'-H,), 5.38–5.53 m (1H, 5-H). Found, %: C 64.30; H 7.61. $C_{16}H_{23}ClO_3$. Calculated, %: C 64.31; H 7.76.

(1*R*)-1-{(1*R*,3*R*,6*S*)-4,7,7-Trimethylbicyclo[4.1.0]-hept-4-en-3-yl}ethyl hydrogen malonate (IIId). A mixture of 0.8 g (0.045 mmol) of alcohol **IIa**, 0.7 g (0.055 mmol) of 2,2-dimethyl-1,3-dioxane-4,6-dione, and 0.1 g of piperidine in 15 ml of toluene was heated for 48 h under reflux. The mixture was washed with a saturated aqueous solution of sodium hydrogen carbonate (3×50 ml), the alkaline extracts were combined and acidified with 10% sulfuric acid to pH 6 on cooling to 3–5°C, and organic acids were extracted into diethyl ether (3×100 ml). After appropriate treatment, we isolated 0.59 g of pure acid **IIId** (according to the TLC and ^1H NMR data). Yield 51%, pale yellow oily substance. ^1H NMR spectrum, δ, ppm: 0.71–0.92 m and 1.13–1.24 m (2H, 1-H, 6-H), 0.87 s and 1.06 s (6H, C^8H_3, C^9H_3), 1.25 d (3H, $C^{2'}H_3$, J = 6.3 Hz), 1.35–1.46 m and 1.67–2.18 m (2H, 2-H), 1.75 s (3H, $C^{10}H_3$), 2.09–2.4 m (1H, 3-H), 3.44 s (2H, $COCH_2$), 4.81–5.4 m (1H, 1'-H), 5.41–5.6 m (1H, 5-H), 8.91 br.s (CO_2H). Found, %: C 67.53; H 8.32. $C_{15}H_{22}O_4$. Calculated, %: C 67.64; H 8.33.

2-{(1*RS*)-[(1*R*,3*R*,6*S*)-4,7,7-Trimethylbicyclo-[4.1.0]hept-4-en-3-yl]ethylamino}ethan-1-ol (IV) (*mixture of diastereoisomers*). Sodium cyanotrihydridoborate, 1 g, was added to a mixture of 2 g (1.12 mmol) of ketone **I** and 1 g of 2-aminoethanol in 10 ml of methanol, and the mixture was stirred for 2 h at room temperature. The mixture was then treated with 10 ml of a saturated aqueous solution of ammonium chloride and extracted with diethyl ether (3× 75 ml). After appropriate treatment, the residue was subjected to chromatography on silica gel using chloroform as eluent to isolate 1.5 g (40%) of compound **IV** as a yellow oily substance. IR spectrum (film), ν, cm^{-1}: 3650, 1715, 1385, 1380, 1655, 880. ^1H NMR spectrum, δ, ppm (major stereoisomer): 0.79–0.98 m and 1.12–1.20 m (2H, 1-H, 6-H), 0.59 s and 0.81 s (6H, C^8H_3, C^9H_3), 1.34 d (3H, $C^{2'}H_3$, J = 7.1 Hz), 1.29–1.40 m and 1.64–1.99 m (2H, 2-H), 1.34 s (3H, $C^{10}H_3$), 2.2–2.39 m (1H, 3-H), 2.9–3.4 m (2H, NH, OH), 3.6–3.9 m (4H, NCH_2CH_2), 4.8–5.23 m (1H, 1'-H), 5.18–5.3 m (1H, 5-H). Found, %: C 75.18; H 11.15; N 6.33. $C_{14}H_{25}NO$. Calculated, %: C 75.28; H 11.28; N 6.27.

***tert*-Butyl *N*-(2-hydroxyethyl)-*N*-{(1*R*,*S*)-[(1*R*,3*R*,6*S*)-4,7,7-trimethylbicyclo[4.1.0]hept-4-en-3-yl]ethyl}-2-aminoacetate (V) (*mixture of diastereoisomers*).** *tert*-Butyl 2-bromoacetate, 1.8 g (0.9 mmol), and potassium carbonate, 0.5 g, were added in succession to a solution of 2 g (0.9 mmol) of amine **IV** in 10 ml of methanol. The mixture was stirred for 48 h at room temperature, 150 ml of chloroform was added, and the mixture was washed with water and subjected to appropriate treatment, followed by chromatography on silica gel. Yield 1.5 g (80%), oily substance. IR spectrum (film), ν, cm^{-1}: 3630, 1715, 1385, 1380, 1655, 880. ^1H NMR spectrum, δ, ppm (major stereoisomer): 0.75–0.93 m and 1.11–1.26 m (2H, 1-H, 6-H), 0.59 s and 0.81 s (6H, C^8H_3, C^9H_3), 1.32 s (9H, CMe_3), 1.34 d (3H, $C^{2'}H_3$, J = 7.1 Hz), 1.29–1.40 m and 1.64–1.99 m (2H, 2-H), 1.34 s (3H, $C^{10}H_3$), 2.0–2.40 m (1H, 3-H), 2.7–3.4 m and 3.4 s (2H, CH_2CO), 3.6–3.9 m (4H, NCH_2CH_2), 4.4–4.93 m (1H, 1'-H), 5.15–5.35 m (1H, 5-H). Found, %: C 71.00; H 10.35; N.09. $C_{20}H_{35}NO_3$. Calculated, %: C 71.18; H 10.45; N 4.15.

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