

Synthesis of Bi- and Tricyclic Monoesters of Dicarboxylic Acids

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Abstract—A thermal addition of aliphatic dicarboxylic acids to bicyclo[2.2.1]-heptene hydrocarbons and to tricyclo[5.2.1.0^{2,6}]deca-3,8-diene was investigated and new samples of dicarboxylic acids alicyclic monoesters were synthesized. Some of monoesters synthesized have a pleasant fragrance and can find application as fragrance substances. They are also of interest as initial components for preparation of new organic compounds.

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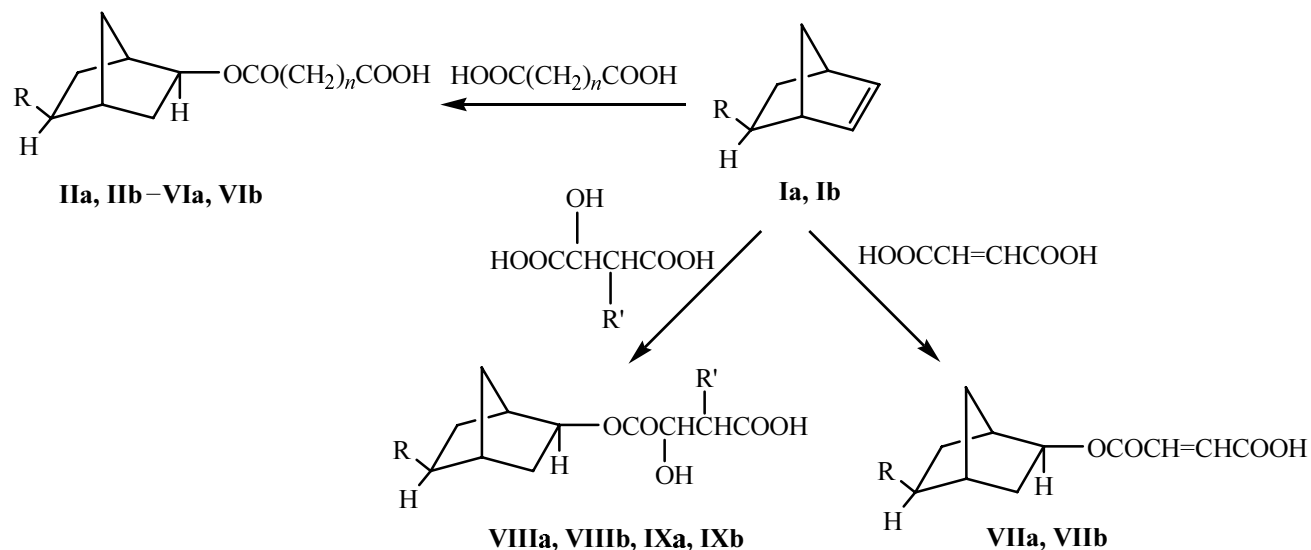
We formerly investigated a thermal addition reaction of aliphatic saturated and unsaturated monocarboxylic acid to bi-, tri-, and tetracyclic olefin hydrocarbons and synthesized the corresponding esters [1–4]. The synthesized 5-methylbicyclo[2.2.1]hept-2-yl, tricyclo[5.2.1.0^{2,6}]-dec-3-en-8(9)yl acetates have a pleasant fragrance and are successfully employed in the fragrance industry for preparation of various compositions [5, 6]. The synthesized unsaturated esters, acrylates, not only have a pleasant odor, but are reactive monomers for preparation of polymers [7].

In the present study we investigated the reaction of dicarboxylic acids from the aliphatic series with bicyclic olefin hydrocarbons and synthesized the corresponding bicyclic monoesters in 70–90% yields.

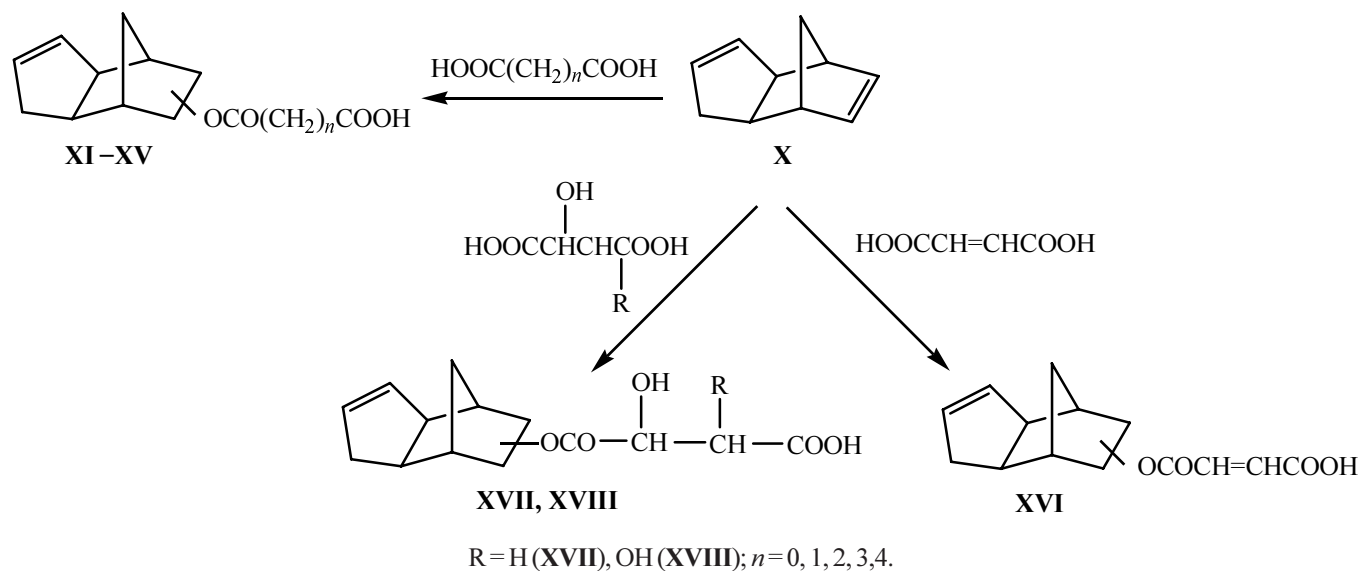
The addition of acids to bicyclic olefins **Ia** and **Ib** proceeded at heating, and the initial acids themselves autocatalyzed the reaction.

Dicarboxylic acids in the same way as monocarboxylic ones add stereo- and regiospecifically to bicyclo[2.2.1]-hept-2-ene (**Ia**) forming *exo*-2-bicyclo[2.2.1]heptyl monoesters [8]. Monoesters prepared from 5-methylbicyclo[2.2.1]hept-2-ene (**Ib**) contain two regioisomers: 90–95% of *exo*-5- and 5–10% of methylbicyclo[2.2.1]-hept-2-yl-*exo*-isomers.

The reaction of saturated and unsaturated, hydroxy-, and dihydroxydicarboxylic acids with *exo*-tricyclo[5.2.1.0^{2,6}]deca-3,8-diene (**X**) was also studied. The initial dicarboxylic acids added exclusively to the π -bond of the



R = H (a), CH₃ (b); R' = H (VIIIa, VIIIb), OH (IXa, IXb); n = 0, 1, 2, 3, 4.



bicycloheptene ring in the molecule of tricyclic hydrocarbon **X**.

The analysis revealed that the dicarboxylic acids stereoselectively added to the tricyclo[5.2.1.0^{2,6}]deca-3,8-diene giving rise to a mixture of two *exo-exo*-regioisomers: tricyclo[5.2.1.0^{2,6}]deca-3-en-8- and tricyclo[5.2.1.0^{2,6}]deca-3-en-9-yl monoesters with the prevalence of the first isomer (92–97%).

By the reaction of maleic, malic, and *d*-tartaric acids with tricyclo[5.2.1.0^{2,6}]deca-3,8-diene the corresponding monoesters were obtained in a 83.9–89.0% yield.

The structure of the obtained bicyclic and tricyclic dicarboxylic acids monoesters was confirmed by an independent synthesis from the corresponding alcohols by their esterification with dicarboxylic acids in the presence of sulfuric acid [9, 10].

The structure of the synthesized monoesters was also proved by the IR and ¹H NMR spectra. The IR spectra contained the characteristic absorption bands of aliphatic dicarboxylic and oxydicarboxylic acids monoesters: 3000–2800 (C–H), 1645 (C=C), 1740 (C=O), 1200–1250 (–O–), and 3500 cm⁻¹ (–OH).

In all ¹H NMR spectra the signal of the *exo*-proton at the C² atom of the bicyclic monoesters appeared in the region 4.6 ppm, the signals of the carboxy group protons at 10.0–11.0 ppm, of the hydroxy group in the spectra if oxyacids monoesters at 2.28 ppm. The protons of the double bond in the spectrum of the maleic acid *exo*-ester gave rise to a multiplet at 6.10–6.25 ppm

Compounds **Ib** and **XIIa** possess a fine pleasant fragrance with a verdure tint and can be used as components for preparation of fragrant compositions.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer UR-20, ¹H MNR spectra were registered on a spectrometer BS-487C (Czechia), operating frequency 80 MHz, internal reference HMDS, solvent CCl₄.

The composition and purity of compounds synthesized and also of initial reagents was analyzed by GLC on a chromatograph LKhM-8MD, column 1500mm long, stationary phase 10 wt% of poly(ethylenglycol succinate) on sferokhrom, carrier gas helium.

The following compounds were used as initial stuff: bicyclo[2.2.1]hept-2-ene (**Ia**), bp 96°C, mp 46°C, purity 99.8% by GLC data; *exo*-5-methylbicyclo[2.2.1]hept-2-ene (**Ib**), bp 115.5°C, d_4^{20} 0.8605, n_D^{20} 1.4600, purity 99% by GLC data; the compounds were prepared by the condensation of cyclopentadiene with ethylene and propylene [11, 12]; *exo*-tricyclo[5.2.1.0^{2,6}]deca-3,8-diene (**X**), bp 170°C (decomp.), mp 19.5°C, d_4^{20} 0.9760, n_D^{20} 1.5051 [13].

Initial dicarboxylic acids were chemically pure substances, and their physical constants were consistent with the published data [14].

The addition of dicarboxylic acids to bicyclic and tricyclic olefins was carried out in a pressure reactor of stainless steel. For homogenization of the initial compounds CCl₄ (38.5 g) was used as solvent, reaction time was 4 h.

Oxalic acid *exo*-bicyclo[2.2.1]hept-2-yl monoester (IIa). A mixture of 47 g of compound **Ia**, 22.5 g of oxalic acid and of solvent was heated at 150°C. The unreacted compound **Ia** and solvent were distilled off in a vacuum, and from the condensate was isolated 41.4 g

(90%) of compound **IIa**, bp 99–100°C (10 mm Hg), d_4^{20} 1.0415, n_D^{20} 1.4690. $^1\text{H NMR}$ spectrum, δ , ppm: 1.0–1.41 d (8H, 4CH₂), 2.20–2.22 m (2H, 2CH), 4.60 d (1H, CH), 10.20 s (1H, COOH). Found, %: C 58.67; H 6.57. C₉H₁₂O₄. Calculated, %: C 58.69; H 6.57.

Oxalic acid *exo*-5-methylbicyclo[2.2.1]hept-2-*exo*-yl monoester (IIb). A mixture of 54 g of compound **Ib**, of oxalic acid and of solvent was heated at 150°C. From the condensate we isolated 44.3 g (89.5%) of compound **IIb**, bp 109–110°C (10 mm Hg), d_4^{20} 1.0186, n_D^{20} 1.4720. Found, %: C 60.58; H 7.11. C₁₀H₁₄O₄. Calculated, %: C 60.60; H 7.12.

Malonic acid *exo*-bicyclo[2.2.1]hept-2-yl monoester (IIIa). From 47 g of compound **Ia** and 26 g of malonic acid at 150°C was obtained 40.6 g (82%) of compound **IIIa**, bp 107–108°C (10 mm Hg), d_4^{20} 1.0315, n_D^{20} 1.4705. $^1\text{H NMR}$ spectrum, δ , ppm: 1.0–1.41 d (8H, 4CH₂), 1.25 t (2H, CH₂), 2.20–2.22 m (2H, 2CH), 4.60 d (1H, CH), 10.0 s (1H, COOH). Found, %: C 60.59; H 7.11. C₁₀H₁₄O₄. Calculated, %: C 60.60; H 7.12.

Malonic acid *exo*-5-methylbicyclo[2.2.1]hept-2-*exo*-yl monoester (IIIb). A mixture of 54 g of compound **Ib** and 26 g of malonic acid was heated at 150°C to obtain 42.9 g (81%) of compound **IIIb**, bp 120–122°C (10 mm Hg), d_4^{20} 1.0170, n_D^{20} 1.4731. Found, %: C 62.25; H 7.58. C₁₁H₁₆O₄. Calculated, %: C 62.26; H 7.59.

Succinic acid *exo*-bicyclo[2.2.1]hept-2-yl monoester (IVa). From 47 g of compound **Ia** and 29.5 g of succinic acid at 150°C was obtained 40.3 g (76.6%) of compound **IVa**, bp 122–123°C (10 mm Hg), d_4^{20} 1.0223, n_D^{20} 1.4760. Found, %: C 62.27; H 7.57. C₁₁H₁₆O₄. Calculated, %: C 62.25; H 7.59.

Succinic acid *exo*-5-methylbicyclo[2.2.1]hept-2-*exo*-yl monoester (IVb). From 54 g of compound **Ib** and 29.5 g of succinic acid at 150°C was obtained 41.5 g (73.4%) of compound **IVb**, bp 133–135°C (10 mm Hg), d_4^{20} 1.0105, n_D^{20} 1.4805. Found, %: C 63.71; H 8.01. C₁₂H₁₈O₄. Calculated, %: C 63.70; H 8.02.

Glutaric acid *exo*-bicyclo[2.2.1]hept-2-yl monoester (Va). From 47 g of compound **Ia** and 33 g of glutaric acid at 150°C was obtained 40.4 g (71.5%) of compound **Va**, bp 133–134°C (10 mm Hg), d_4^{20} 1.02001, n_D^{20} 1.4718. Found, %: C 63.70; H 8.01. C₁₂H₁₈O₄. Calculated, %: C 63.71; H 8.02.

Glutaric acid *exo*-5-methylbicyclo[2.2.1]hept-2-*exo*-yl monoester (Vb). From 54 g of compound **Ib** and 33 g of glutaric acid at 150°C we obtained 43.2 g (72%) of compound **Vb**, bp 130–132°C (5 mm Hg), d_4^{20} 1.0095, n_D^{20} 1.4810. Found, %: C 64.97; H 8.36. C₁₃H₂₀O₄. Calculated, %: C 64.98; H 8.39.

Adipic acid *exo*-bicyclo[2.2.1]hept-2-yl monoester (VIa). A mixture 47 g of compound **Ia**, 36.5 g of adipic acid and of solvent was heated at 160°C. We obtained 42 g (70%) of compound **VIa**, bp 142–143°C (10 mm Hg), d_4^{20} 1.02091, n_D^{20} 1.4728. Found, %: C 64.97; H 8.36. C₁₃H₂₀O₄. Calculated, %: C 64.98; H 8.38.

Adipic acid *exo*-5-methylbicyclo[2.2.1]hept-2-*exo*-yl monoester (VIb). From 54 g of compound **Ib** and 36.5 g of adipic acid at 160°C was obtained 44.4 g (70%) of compound **VIb**, bp 145–147°C (5 mm Hg), d_4^{20} 1.0052, n_D^{20} 1.4822. Found, %: C 66.11; H 8.71. C₁₄H₂₂O₄. Calculated, %: C 66.12; H 8.72.

Maleic acid *exo*-bicyclo[2.2.1]hept-2-yl monoester (VIIa). From 47 g of compound **Ia** and 29 g of maleic acid at 130°C we obtained 48.3 g (92%) of compound **VIIa**, bp 121–122°C (5 mm Hg), d_4^{20} 1.0191, n_D^{20} 1.4798. $^1\text{H NMR}$ spectrum, δ , ppm: 1.1–1.41 d (8H, 4CH₂), 2.20–2.21 m (2H, 2CH), 4.60 d (1H, CH), 6.0–6.2 m (2H, 2CH=), 10.10 s (1H, COOH). Found, %: C 62.83; H 6.70. C₁₁H₁₄O₄. Calculated, %: C 62.85; H 6.71.

Maleic acid *exo*-5-methylbicyclo[2.2.1]hept-2-*exo*-yl monoester (VIIb). From 54 g of compound **Ib** and 29 g of maleic acid at 130°C we obtained 49.2 g (88%) of compound **VIIb**, bp 132–135°C (5 mm Hg), d_4^{20} 1.0102, n_D^{20} 1.4858. Found, %: C 64.26; H 7.18. C₁₂H₁₆O₄. Calculated, %: C 64.28; H 7.19.

3-Hydroxysuccinic acid *exo*-bicyclo[2.2.1]hept-2-yl monoester (VIIIa). From 47 g of compound **Ia** and 33.5 g of malic acid at 150°C we obtained 54.1 g (95%) of compound **VIIIa**, bp 123–124°C (5 mm Hg), d_4^{20} 1.0101, n_D^{20} 1.4690. Found, %: C 57.86; H 7.05. C₁₁H₁₆O₅. Calculated, %: C 57.89; H 7.06.

3-Hydroxysuccinic acid *exo*-5-methylbicyclo[2.2.1]hept-2-*exo*-yl monoester (VIIIb). From 54 g of compound **Ib** and 33.5 g of malic acid at 150°C we obtained 55.9 g (92.5%) of compound **VIIIb**, bp 132–135°C (5 mm Hg), d_4^{20} 1.1065, n_D^{20} 1.4635. Found, %: C 59.47; H 7.47. C₁₂H₁₈O₅. Calculated, %: C 59.48; H 7.48.

***d*-Tartaric acid *exo*-bicyclo[2.2.1]hept-2-yl monoester (IXa).** From 47 g of compound **Ia** and 37.5 g of *d*-tartaric acid at 150°C we obtained 58.2 g (93.5%) of compound **IXa**, bp 131–132°C (5 mm Hg), d_4^{20} 1.0305, n_D^{20} 1.4695. Found, %: C 54.07; H 6.58. C₁₁H₁₆O₆. Calculated, %: C 54.09; H 6.60.

***d*-Tartaric acid *exo*-5-methylbicyclo[2.2.1]hept-2-*exo*-yl monoester (IXb).** From 54 g of compound **Ib** and 37.5 g of *d*-tartaric acid at 150°C we obtained 58 g (90%) of compound **IXb**, bp 148–150°C (5 mm Hg), d_4^{20}

1.1025, n_D^{20} 1.4790. Found, %: C 55.78; H 7.01. $C_{12}H_{18}O_6$. Calculated, %: C 55.80; H 7.02.

Oxalic acid *exo*-tricyclo[5.2.1.0^{2,6}]dec-3-en-8(9)-*exo*-yl monoester (XI). From 66 g of compound **X** and 22.5 g of oxalic acid at 140°C we obtained 53.8 g (97%) of compound **XI**, bp 68–69°C (2 mm Hg), d_4^{20} 1.0262, n_D^{20} 1.5109. Found, %: C 64.73; H 6.22. $C_{12}H_{14}O_4$. Calculated, %: C 64.86; H 6.35.

Malonic acid *exo*-tricyclo[5.2.1.0^{2,6}]dec-3-en-8(9)-*exo*-yl monoester (XII). From 66 g of compound **X** and 26 g of malonic acid at 140°C we obtained 47.8 g (81%) of compound **XII**, bp 78–80°C (2 mm Hg), d_4^{20} 1.0181, n_D^{20} 1.5208. Found, %: C 66.00; H 6.61. $C_{13}H_{16}O_4$. Calculated, %: C 66.08; H 6.82.

Succinic acid *exo*-tricyclo[5.2.1.0^{2,6}]dec-3-en-8(9)-*exo*-yl monoester (XIII). From 66 g of compound **X** and 29.5 g of succinic acid at 140°C we obtained 48.9 g (78.3%) of compound **XIII**, bp 86–87°C (2 mm Hg), d_4^{20} 1.0113, n_D^{20} 1.5261. Found, %: C 67.10; H 7.09. $C_{14}H_{18}O_4$. Calculated, %: C 67.18; H 7.25.

Glutaric acid *exo*-tricyclo[5.2.1.0^{2,6}]dec-3-en-8(9)-*exo*-yl monoester (XIV). From 66 g of compound **X** and 33 g of glutaric acid at 140°C we obtained 50.3 g (76.2%) of compound **XIV**, bp 97–100°C (2 mm Hg), d_4^{20} 1.0080, n_D^{20} 1.5282. Found, %: C 68.05; H 7.46. $C_{15}H_{20}O_4$. Calculated, %: C 68.17; H 7.62.

Adipic acid *exo*-tricyclo[5.2.1.0^{2,6}]dec-3-en-8(9)-*exo*-yl monoester (XV). From 66 g of compound **X** and 36.5 g of adipic acid at 140°C we obtained 50.1 g (72.1%) of compound **XV**, bp 105–108°C (2 mm Hg), d_4^{20} 1.0075, n_D^{20} 1.5298. Found, %: C 68.89; H 7.85. $C_{16}H_{22}O_4$. Calculated, %: C 69.05; H 7.97.

Maleic acid *exo*-tricyclo[5.2.1.0^{2,6}]dec-3-en-8(9)-*exo*-yl monoester (XVI). From 66 g of compound **X** and 29 g of maleic acid at 130°C we obtained 55.9 g (90.2%) of compound **XVI**, bp 85–88°C (2 mm Hg), d_4^{20} 1.1122, n_D^{20} 1.5185. ¹H NMR spectrum, δ , ppm: 1.45 m (2H, CH₂), 2.0–2.25 m (4H, 2CH₂), 2.25–2.30 d (2H, 2CH), 2.50–2.60 m (2H, 2CH), 4.80–4.88 q (2H, 2CH=), 5.90 d (1H, CH), 6.10–6.25 m (2H, 2CH=), 10.12 s (1H, COOH). Found, %: C 67.64; H 6.36. $C_{14}H_{16}O_4$. Calculated, %: C 67.72; H 6.49.

3-Hydroxysuccinic acid *exo*-tricyclo[5.2.1.0^{2,6}]dec-3-en-8(9)-*exo*-yl monoester (XVII). From 66 g of compound **X** and 33.5 g of malic acid at 140°C we obtained 55.8 g (83.9%) of compound **XVII**, bp 119–121°C (2 mm Hg), d_4^{20} 1.2015, n_D^{20} 1.5201. Found, %: C 63.01; H 6.66. $C_{14}H_{18}O_5$. Calculated, %: C 63.15; H 6.81.

***d*-Tartaric acid *exo*-tricyclo[5.2.1.0^{2,6}]dec-3-en-8(9)-*exo*-yl monoester (XVIII).** From 66 g of compound **X** and 37.5 g of *d*-tartaric acid at 140°C we obtained 62 g (88%) of compound **XVIII**, bp 145–147°C (2 mm Hg), d_4^{20} 1.2111, n_D^{20} 1.5107. Found, %: C 59.48; H 6.25. $C_{14}H_{18}O_6$. Calculated, %: C 59.56; H 6.43.

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