

Synthesis of 2-(Bicyclo[2.2.1]hept-2-yloxy)ethyl Carboxylates

A. G. Gasanov and A. V. Nagiev

Institute of Petrochemical Processes, National Academy of Sciences of Azerbaidjan,
pr. Khodzhalı 30, Baku, 370025 Azerbaidjan

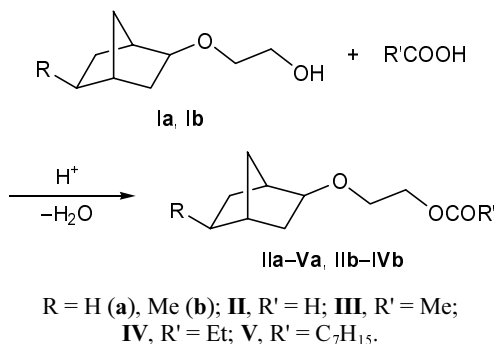
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Abstract—Esterification of aliphatic carboxylic acids with 2-(bicyclo[2.2.1]hept-2-yloxy)ethanol and 2-(5-methylbicyclo[2.2.1]hept-2-yloxy)ethanol in the presence of KU-2-8 cation exchanger (H^+ form) afforded a series of new compounds containing both ester and ether moieties.

Synthesis and applications of alicyclic ethers and esters were extensively studied [1–3]. We previously reported on acid-catalyzed addition of aliphatic mono- and dibasic alcohols to bicyclo[2.2.1]hept-2-enes [4], which led to formation of ethylene glycol bicycloalkyl monoethers **Ia** and **Ib**. Ethers **Ia** and **Ib** possess two osmophoric functional groups which endow these compounds with a specific odor. Such ethers can be used as components of fragrant compositions.

With a view to elucidate how replacement of the hydroxy group in molecules **Ia** and **Ib** by ester will affect their aromatic properties, we brought these compounds into reactions with fatty aromatic acids and obtained new products containing both ether and ester moieties (Scheme 1). In going from formic to acetic, propionic, and octanoic acids, the yield of the corresponding esters decreases from 80.4 to 50.5%, but it does not depend on the presence of a methyl group in the bicyclo[2.2.1]heptane fragment.

Scheme 1.



Initial ethylene glycol monoethers **Ia** and **Ib**, as well as esterification products **II–V**, are *exo* isomers. Compounds **IIb–IVb** are mixtures of 97.5–98.0% of *exo*-2,5 and 2.0–2.5% of *exo*-2,6 isomers. The purity

of the products isolated by distillation was 99.0–99.8%. Their isomeric composition and structure were studied by GLC and IR and NMR spectroscopy. In the IR spectra we observed absorption bands at 1730–1740 and 1125–1130 cm^{-1} due to ester carbonyl and ether moiety, respectively. The ¹³C NMR spectra contained signals from carbon atoms in the norbornane skeleton, attached to ether oxygen, and downfield signals from the ester carbonyl carbon atom (δ_C 169.6–170.3 ppm).

Bicycloalkyl esters on the basis of norbornene and 2-methylnorbornene were recommended for use as components of fragrant compositions [5].

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer in the range from 4000 to 700 cm^{-1} . The ¹³C NMR spectra were measured on a Varian FT-80 instrument (20 MHz) using dioxane as solvent. Gas-liquid chromatography was performed on an LKhM-8MD chromatograph (stationary phase 10% of polyethylene glycol succinate on Sferokrom; column length 2 m; oven temperature 120°C; carrier gas helium, flow rate 45 ml/min).

Initial compounds **Ia** and **Ib** were prepared by addition of ethylene glycol to the corresponding bicyclo[2.2.1]hept-2-enes [4]. Reactions of carboxylic acids with alcohols **Ia** and **Ib** were performed according to a standard procedure in the presence of KU-2-8 cation exchanger (H^+ form); benzene was used as solvent (for removal of liberated water as azeotrope) in an amount equal to the overall volume of the reactants.

2-(Bicyclo[2.2.1]hept-*exo*-2-yloxy)ethyl formate (IIa). A mixture of 31.2 g of 2-(bicyclo[2.2.1]hept-*exo*-2-yloxy)ethanol, 14.2 g of formic acid, and KU-2-8

cation exchanger (5 wt % of the overall amount of the reactants) in 45 ml of benzene was heated for 3–4 h under continuous stirring in a flask equipped with a Dean–Stark trap. The catalyst was filtered off, and the product was isolated by fractional distillation under reduced pressure. Yield 28.9 g (78.5%), bp 106–108°C (20 mm), $n_D^{20} = 1.4676$, $d_4^{20} = 1.0795$. ^{13}C NMR spectrum, δ_{C} , ppm: 170.3 (C¹⁰), 86.3 (C²), 70.8 (C⁹), 41.1 (C¹), 39.6 (C⁴), 35.5 (C³), 28.3 (C⁶), 26.2 (C⁷), 24.9 (C⁵). Found, %: C 65.19; H 8.66. C₁₀H₁₆O₃. Calculated, %: C 65.22; H 8.69.

Compounds **IIIa–Va** and **IIb–IVb** were synthesized in a similar way.

2-(Bicyclo[2.2.1]hept-*exo*-2-yloxy)ethyl acetate (IIIa). Yield 70%, bp 109–110°C (10 mm), $n_D^{20} = 1.4647$, $d_4^{20} = 1.0563$. ^{13}C NMR spectrum, δ_{C} , ppm: 169.4 (C¹⁰), 85.6 (C²), 70.6 (C⁹), 70.0 (C⁸), 41.2 (C¹), 39.9 (C⁴), 36.9 (C³), 28.8 (C⁶), 26.0 (C⁷), 24.0 (C⁵), 17.9 (C¹¹). Found, %: C 66.64; H 9.06. C₁₁H₁₈O₃. Calculated, %: C 66.66; H 9.09.

2-(Bicyclo[2.2.1]hept-*exo*-2-yloxy)ethyl propionate (IVa). Yield 64.4%, bp 127–129°C (10 mm), $n_D^{20} = 1.4612$, $d_4^{20} = 1.0285$. ^{13}C NMR spectrum, δ_{C} , ppm: 169.2 (C¹⁰), 85.6 (C²), 70.2 (C⁹), 70.0 (C⁸), 41.2 (C¹), 39.3 (C⁴), 36.5 (C³), 28.2 (C⁶), 27.6 (C¹¹), 27.2 (C⁷), 24.9 (C⁵), 17.8 (C¹²). Found, %: C 37.90; H 9.40. C₁₂H₂₀O₃. Calculated, %: C 67.92; H 9.43.

2-(Bicyclo[2.2.1]hept-*exo*-2-yloxy)ethyl octanoate (Va). Yield 50.5%, bp 140–145°C (1 mm), $n_D^{20} = 1.4545$, $d_4^{20} = 0.9638$. ^{13}C NMR spectrum, δ_{C} , ppm: 167.4 (C¹⁰), 83.1 (C²), 70.3 (C⁹), 67.6 (C⁸), 41.0 (C¹), 39.9 (C⁴), 36.9 (C³), 29.2 (C⁶), 27.6 (C⁷), 27.4 (C¹¹), 26.5 (C¹²), 26.4 (C¹³), 26.1 (C¹⁴), 22.3 (C¹⁵), 20.0 (C¹⁶), 16.7 (C¹⁷). Found, %: C 69.35; H 10.18. C₁₇H₃₀O₃. Calculated, %: C 69.39; H 10.20.

2-(5-Methylbicyclo[2.2.1]hept-*exo*-2-yloxy)ethyl formate (IIb). Yield 80.4%, bp 76–78°C (3 mm), $n_D^{20} = 1.4615$, $d_4^{20} = 1.0447$. ^{13}C NMR spectrum, δ_{C} , ppm: 169.7 (C¹⁰), 86.2 (C²), 70.6 (C⁹), 70.0 (C⁸), 42.2 (C¹), 38.7 (C⁴), 35.6 (C³), 33.4 (C⁷), 30.4 (C⁵), 27.7 (C⁶), 15.3 (C¹¹). Found, %: C 66.62; H 9.07. C₁₁H₁₈O₃. Calculated, %: C 66.66; H 9.09.

2-(5-Methylbicyclo[2.2.1]hept-*exo*-2-yloxy)ethyl acetate (IIIb). Yield 12.6%, bp 100–105°C (3 mm), $n_D^{20} = 1.4605$, $d_4^{20} = 1.0287$. ^{13}C NMR spectrum, δ_{C} , ppm: 169.0 (C¹⁰), 85.4 (C²), 70.5 (C⁹), 70.2 (C⁸), 42.0 (C¹), 39.4 (C⁴), 36.2 (C³), 35.2 (C⁷), 30.8 (C⁵), 28.5 (C⁶), 20.1 (C¹¹), 17.1 (C¹²). Found, %: C 67.88; H 9.41. C₁₂H₂₀O₃. Calculated, %: C 67.92; H 9.43.

2-(5-Methylbicyclo[2.2.1]hept-*exo*-2-yloxy)ethyl propionate (IVb). Yield 65.0%, bp 120–125°C (2 mm), $n_D^{20} = 1.4590$, $d_4^{20} = 1.0050$. ^{13}C NMR spectrum, δ_{C} , ppm: 168.7 (C¹⁰), 85.2 (C²), 70.3 (C⁹), 70.1 (C⁸), 42.0 (C¹), 39.5 (C⁴), 36.2 (C³), 32.2 (C⁷), 30.0 (C⁵), 28.7 (C⁶), 26.6 (C¹¹), 20.0 (C¹²), 17.2 (C¹³). Found, %: C 69.01; H 9.70. C₁₃H₂₂O₃. Calculated, %: C 69.03; H 9.73.

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