

Esters Synthesis by Addition of Monocarboxylic Acids to *exo*-5-Substituted Bicyclo[2.2.1]hept-2-ene Hydrocarbons

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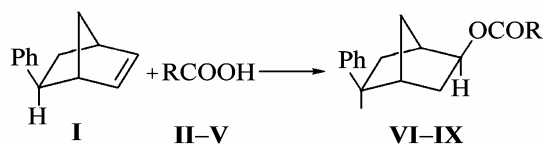
Abstract—New alicyclic esters were synthesized by addition at heating of aliphatic monocarboxylic saturated acids C_1 – C_4 to *exo*-5-phenyl-, *exo*-5-cyclohexyl-, and *exo*-5-(cyclohex-3-enyl)bicyclo[2.2.1]hept-2-enes. Among the esters obtained the acetates has more pleasant odor with fruit tint, and they may be used as a component of synthetic perfumes.

We have previously developed efficient procedures for preparation of esters of alicyclic alcohols by adding aliphatic saturated monocarboxylic acids to bicyclo[2.2.1]hept-2-ene, tricyclo[5.2.1.0^{2,6}]deca-3,8-diene, tetracyclo-[4.4.1^{2,5}.1^{7,10}.0^{1,6}]dodec-3-ene hydrocarbons and to their derivatives [1–4]. The esters “Menorat” and “Dicilat” thus prepared are applied with success for industrial preparation of synthetic perfumes [5, 6].

Aiming at increasing the range of available synthetic perfumes in continuation of the study on preparation of new esters of alicyclic alcohols we investigated the addition of aliphatic saturated monocarboxylic acids to some derivatives of bicyclo[2.2.1]hept-2-ene hydrocarbons.

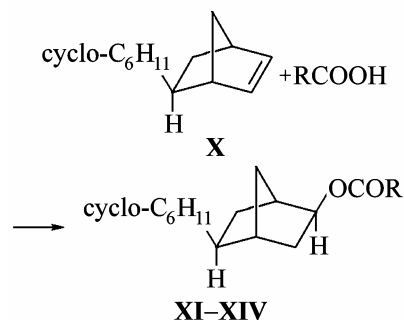
It was established that saturated aliphatic monocarboxylic acids C_1 – C_4 add without catalyst (mineral or Lewis acids) at heating to 120–190°C to *exo*-5-substituted bicycloolefins affording the corresponding esters.

As a derivative of a bicycloolefin was used *exo*-5-phenylbicyclo[2.2.1]hept-2-ene, and therefrom were synthesized in 65.6–78.5% yields esters of *exo*-5-phenylbicyclo[2.2.1]hetan-*exo*-2-ol VI–IX.



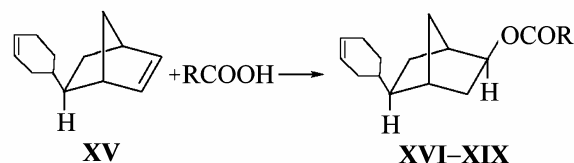
To evaluate the effect of substituents at the bicycloolefin *exo*-5-cyclohexylbicyclo[2.2.1]hept-2-ene

was used as initial component in reaction with monocarboxylic acids. It was established that the addition of acid to the double bond of the bicycloolefin occurred with greater regioselectivity and with higher yield than at the use of *exo*-5-phenylbicyclo[2.2.1]hept-2-ene.



In both reaction alongside the main products, esters of *exo*-5-phenyl- and *exo*-5-cyclohexylbicyclo[2.2.1]hetan-*exo*-2-ol (95–98%) were obtained as side products their regioisomers, *exo*-6-phenyl- and *exo*-6-cyclohexylbicyclo[2.2.1]hetan-*exo*-2-ol in 4–5 and 2–3% respectively.

The thermal addition of monocarboxylic acids C_1 – C_4 was also carried out with *exo*-5-(cyclohex-3-enyl)bicyclo[2.2.1]hept-2-ene. It was established that only the double bond of the bicyclo[2.2.1]hept-2-ene system added the acid molecule, and the π -bond of the cyclohexyl ring remained intact.



The purity and isomer composition of esters **XVI-XIX** was evaluated by GLC. It was found that to 95-97% the mixture consisted of *exo*-5-(cyclohex-3-enyl)bicyclo[2.2.1]heptan-*exo*-2-ol and to 3-5% of *exo*-6-(cyclohex-3-enyl)bicyclo-[2.2.1]heptan-*exo*-2-ol

It was therefore proved that aliphatic saturated monocarboxylic acids added to *exo*-5-substituted bicyclo[2.2.1]hept-2-ene hydrocarbons furnishing *exo*-stereoisomeric esters.

Both in the previous and this study we proved that the substituents of bicyclo[2.2.1]hept-2-ene molecule direct addition of the acyloxy group mainly to C² atom with formation of 5- and 2-substituted derivatives.

The structure of esters synthesized was proved by IR and ¹H NMR spectroscopy.

In the IR spectra of all compounds obtained appear strong absorption bands in the region 1740–1730 and 1250–1200 cm⁻¹ characteristic of C=O and C-O-C groups in ester molecules. The bands at 775, 700, and 1640 cm⁻¹ correspond in the spectra of esters **VI-IX** and **XVI-XIX** respectively to bending vibrations of monosubstituted benzene ring and of the double bond in the cyclohexene ring. In all IR spectra except those of formates (in the spectra of acetates, propionates, and butyrates) appear absorption bands in the region 1380 and 2870 cm⁻¹ indicating the presence of a methyl group.

The signals at δ 4.60-4.80 ppm in the ¹H NMR spectra confirm formation of *exo,exo*-isomers of esters, and the signal at δ 8.20-7.80 ppm belongs to the proton of formyloxy group in formates.

In the ¹³C NMR spectra the signals of ester group carbons in formates, acetates, and propionates appear in the region δ 157.3–169.6 ppm.

The structure of compounds synthesized was confirmed by independent synthesis. Hydrogenation of *exo*-5-phenylbicyclo[2.2.1]heptyl *exo*-2-acetate and also of *exo*-5-(cyclohex-3-enyl)bicyclo[2.2.1]heptyl *exo*-2-acetate under hydrogen pressure of 80-100 at catalyzed by Ni on Kieselgur furnished *exo*-5-cyclohexylbicyclo[2.2.1]heptyl *exo*-2-acetate (**XII**). The physical constants of samples obtained by different methods were identical.

The esters synthesized are new organic compounds, transparent colorless fluids; among them acetates, especially *exo*-5-cyclohexylbicyclo-[2.2.1]-heptyl *exo*-acetate, have more pleasant and fragrant odors with fruit tint and may be used as components of synthetic perfumes.

EXPERIMENTAL

IR spectra were recorded on spectrophotometer UR-20 from thin films. ¹H and ¹³C NMR spectra were registered on spectrometer Varian FT-80 at operating frequency 80 MHz from solutions in carbon tetrachloride.

Composition and purity of esters synthesized was analyzed by GLC on chromatograph LKhM-8 MD, stationary phase 10 wt% of polyethylene glycol succinate on INZ-600 carrier, column 1000 × 3 mm, oven temperature 160°C, vaporizer temperature 250°C, detector current 120 mA, carrier gas helium, flow rate 45 ml min⁻¹.

Fractional distillation in a vacuum with a Vigreux column of 15 cm long provided the esters synthesized in 99.5-99.7% purity.

As initial compounds were used *exo*-5-phenylbicyclo[2.2.1]hept-2-ene (**I**), bp 135-136°C (9 mm Hg), d_4^{20} 1.0270, n_D^{20} 1.5480; *exo*-5-cyclohexylbicyclo[2.2.1]hept-2-ene (**X**), bp 100-101°C (4 mm Hg), d_4^{20} 0.9695, n_D^{20} 1.5120; *exo*-5-(cyclohex-3-yl)bicyclo[2.2.1]hept-2-ene (**XV**), bp 100-102°C (4 mm Hg), d_4^{20} 0.9760, n_D^{20} 1.5104.

Hydrocarbons **I**, **X**, **XV** were prepared by 4+2 cycloaddition of cyclopentadiene to styrene, vinylcyclohexane, and 4-vinylcyclohexene respectively along procedure from [8, 9]. The resulting product contained a mixture of *endo*- and *exo*- isomers that was converted into an individual *exo*-isomer by method [10].

Initial aliphatic monocarboxylic acids were commercial products: formic acid (State Standard GOST 5848-73), acetic acid (State Standard GOST 61-75), propionic acid (Production Certificate TU 6-09.1684-72), and butyric acid (Production Certificate TU 6-09.530-75). The acids before use were subjected to distillation, and afterwards their physical constant coincided with the published data[11].

The reaction of acid addition to bicyclo-[2.2.1]hept-2-ene hydrocarbons **I**, **V**, **XV** was carried out in a pressure reactor at molar ratio acid : hydrocarbon 5 : 1. The mixture was heated to 120-190°C for 3 h.

exo-5-Phenylbicyclo[2.2.1]heptyl *exo*-2-formate (**VI**). A mixture of 17.0 g of compound **I** and 23.0 g of formic acid was heated to 120°C for 3 h. On distilling

Yields, physical constants, and elemental analyses of esters of *exo*-5-phenyl-, *exo*-5-cyclohexyl-, and *exo*-5-(cyclohex-3-enyl)bicyclo[2.2.1]heptan-*exo*-2-ols

Compd. no.	Yield, %	bp, °C (mm Hg)	d_4^{20}	n_D^{20}	Found, %		Formula	Calculated, %	
					C	H		C	H
VI	78.5	150–152	1.1617	1.5460	77.71	7.43	C ₁₄ H ₁₆ O ₂	77.74	7.46
VII	75.0	168–170	1.1116	1.5310	78.19	7.85	C ₁₅ H ₁₈ O ₂	78.21	7.89
VIII	70.1	182–184	1.0941	1.5345	78.61	8.24	C ₁₆ H ₂₀ O ₂	78.65	8.25
IX	65.6	195–197	1.0635	1.5368	79.01	8.56	C ₁₇ H ₂₂ O ₂	79.03	8.58
XI	90.0	142–144	1.0701	1.5142	75.60	9.94	C ₁₄ H ₂₂ O ₂	75.64	9.97
XII	85.5	163–164	1.0503	1.5039	76.20	10.21	C ₁₅ H ₂₄ O ₂	76.23	10.24
XIII	80.1	174–176	1.0465	1.5060	76.71	10.42	C ₁₆ H ₂₆ O ₂	76.75	10.47
XIV	75.6	190–192	1.0328	1.5069	77.20	10.63	C ₁₇ H ₂₈ O ₂	77.23	10.67
XVI	82.8	145–148	1.0749	1.5154	76.30	9.12	C ₁₄ H ₂₀ O ₂	76.33	9.15
XVII	78.4	165–167	1.0613	1.5061	76.85	9.43	C ₁₅ H ₂₂ O ₂	76.88	9.46
XVIII	75.6	178–179	1.0470	1.5070	77.35	9.71	C ₁₆ H ₂₄ O ₂	77.38	9.74
XIX	69.0	191–192	1.0343	1.5085	77.80	9.96	C ₁₇ H ₂₆ O ₂	77.82	9.99

off excess formic acid at atmospheric pressure and fractionation of the residue in a vacuum was isolated 16.9 g of compound VI.

Esters VII–IX were prepared in a similar way.

Exo-5-Cyclohexylbicyclo[2.2.1]heptyl *exo*-2-acetate (XII). A mixture of 35.2 g of compound X and 60.0 g of acetic acid was heated to 170°C for 3 h. On distilling off excess acetic acid at atmospheric pressure and fractionation of the residue in a vacuum was isolated 40.3 g of compound XII.

Esters XI, XIII, XIV were prepared in a similar way.

Exo-5-(Cyclohex-3-enyl)bicyclo[2.2.1]heptyl *exo*-2-propionate (XVIII). A mixture of 17.4 g of compound XV and 37.0 g of propionic acid was heated to 180°C for 3 h. On distilling off excess propionic acid at atmospheric pressure and fractionation of the residue in a vacuum was isolated 40.3 g of compound XVIII.

Esters XVI, XVII, XIX were prepared in a similar way.

Physical characteristics and elemental analyses of esters synthesized are listed in table.

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