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Synthesis of Saturated Bicyclic Diesters

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Abstract—Bicyclic saturated diesters were synthesized by the catalytic addition of monobasic saturated acids to unsaturated bicyclic esters. A possible mechanism of the reaction was proposed.

Keywords: bicyclic diesters, saturated acids, (bicyclo[2.2.1]hept-2-ene-5-yl) acetates

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Bicyclic diesters are being used to success in many fields as, for example, polymer plasticizers [1, 2], lubricant oils [3], as well as components of synthetic fragnances [4].

The main methods of synthesis of diesters derived from bicyclic diols include esterification reactions in the presence of various homogeneous acid catalysts [5], as well as reactions of aliphatic acid anhydrides with unsaturated bicyclic alcohols [6]. The starting materials for these reactions are either hardly accessible diols or rather costly acid anhydrides.

In the present work, we have demonstrated the possibility to synthesize bicyclic diesters by a reaction not involving diols, specifically, by the catalytic addition of monobasic saturated acids to unsaturated bicyclic monoesters.

Aiming at the synthesis of diesters derived from bicyclo [2.2.1]heptane-2,5-diol and (2-hydroxybicyclo-[2.2.1]hept-5-yl)methanol we have studied the addition of saturated acids to (bicyclo[2.2.1]hept-2-ene-5-yl) acetate and (bicyclo[2.2.1]hept-2-ene-5-yl)methyl acetate. The addition of saturated acids to methyl and ethyl (bicyclo[2.2.1]hept-2-ene-5-carboxylates and their 5-methyl derivatives in the presence of boron trifluoride etherate, yielding diesters of norbornane oxoacids.

The reactions of saturated acids with unsaturated bicyclic monoesters **1–6** (molar ratio 2 : 1) in the presence of boron trifluoride etherate (0.1 wt % per saturated acid) occurred at 80°C for 3 h to form bicyclic diesters **7–42** in yields of 61–95% (Scheme 1). According to GLC analysis, the synthesized compounds are mixtures of two regioisomers (2,5 and 3,5), containing 91.0–95.0% of the 2,5 derivatives. The yields, physicochemical characteristics, and elemental analyses of the products are listed in the table. The regioisomers had close boiling points and were impossible to separate by vacuum distillation; therefore, they were characterized as a mixture.

The structure of compounds **7–42** was confirmed by IR and NMR spectroscopy. Thus, the IR spectra show no C=C absorption band 1640 cm^{-1}, which is observed in the spectra of the starting unsaturated bicyclic monoesters **1–6**. This finding suggests that the synthesized compounds have a saturated bicyclic ring and are diesters.

According to the ^{1}H and ^{13}C data, saturated acids add to unsaturated bicyclic monoetsres in a stereoselective fashion to form an *exo* isomer. The ^{1}H NMR spectrum contains signals at 4.10–4.20 ppm, assignable to *exo* protons.

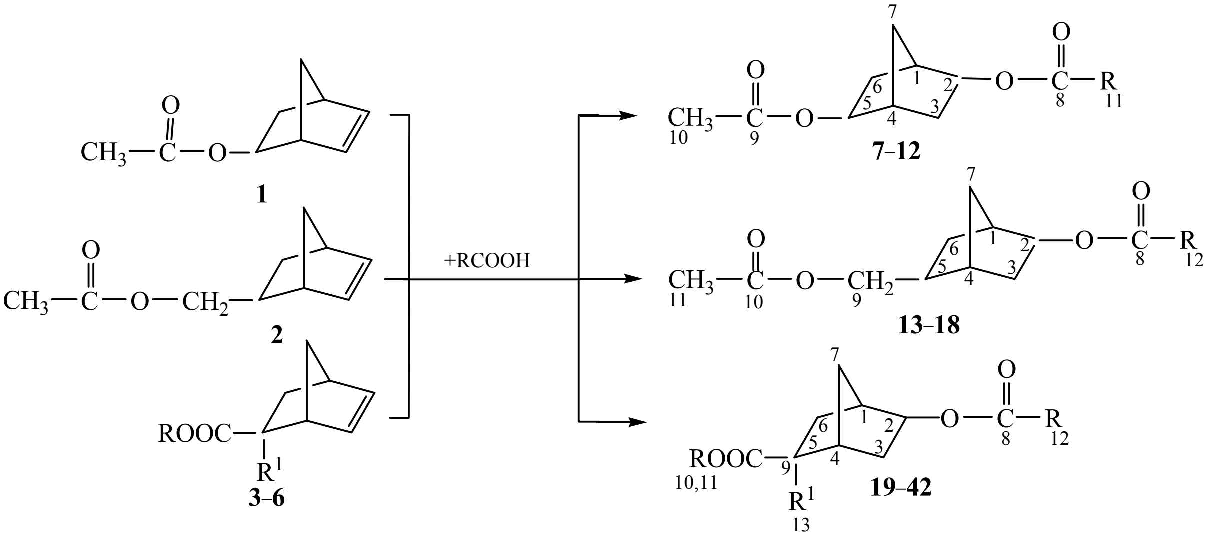
It was found that the yield of bicyclic esters decreases with increasing hydrocarbon chain length in the parent saturated acids: $HCOOH > CH_3COOH > CH_3CH_2COOH > CH_3CH_2CH_2COOH > CH_3CH_2CH_2CH_2COOH$. This regularity can be explained by the decreasing dissociation degree and activity of the saturated acids. The yield of bicyclic diesters from isobutyric acid is lower than from butyric acid.

Scheme 2 presents the proposed mechanism of the $BF_3{\cdot}OEt_2$-catalyzed addition reaction.

Yields, boiling points, and elemental analyses of bicyclic esters **7–42**

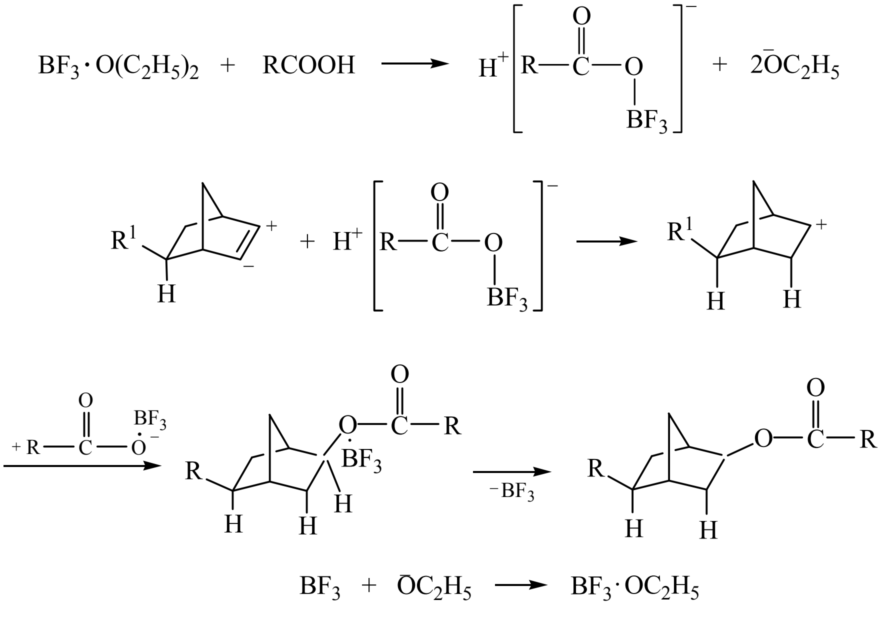
Comp. no.	Yield, %	bp, °C (2 mmHg)	Contents of regioisomers by GLC, %		Found, %		Formula	Calculated, %	
			2,5	3,5	C	H		C	H
7	92.0	104–105	95.1	4.9	60.32	7.10	$C_{10}H_{14}O_4$	60.59	7.11
8	87.0	110–111	94.9	5.1	62.01	7.38	$C_{11}H_{16}O_4$	62.24	7.59
9	84.5	118–120	94.5	5.5	63.43	8.00	$C_{12}H_{18}O_4$	63.69	8.01
10	80.6	128–129	94.2	5.8	64.91	8.18	*p*-$C_{13}H_{20}O_4$	64.97	8.38
11	78.4	112–114	94.2	5.8	64.38	8.01	*i*-$C_{13}H_{20}O_4$	64.97	8.39
12	73.6	138–139	93.7	6.3	66.00	8.88	$C_{14}H_{22}O_4$	66.11	8.71
13	94.9	117–118	94.8	5.2	62.01	7.50	$C_{11}H_{16}O_4$	62.20	7.54
14	93.4	127–128	94.2	4.8	63.51	7.93	$C_{12}H_{18}O_4$	63.66	7.95
15	90.1	140–142	93.7	6.3	64.91	8.22	$C_{13}H_{20}O_4$	64.94	8.32
16	85.4	152–153	93.3	6.7	66.00	8.61	*p*-$C_{14}H_{22}O_4$	66.08	8.65
17	80.5	145–146	93.3	6.7	67.02	8.92	*i*-$C_{14}H_{22}O_4$	67.11	8.98
18	82.8	164–165	92.2	7.8	68.01	9.15	$C_{15}H_{24}O_4$	68.03	9.21
19	92.0	65–66	93.5	6.5	60.33	7.00	$C_{10}H_{14}O_4$	60.61	7.07
20	88.0	70–71	93.2	6.8	62.01	7.39	$C_{11}H_{16}O_4$	62.24	7.59
21	78.5	110–112	93.0	7.0	63.48	8.01	$C_{12}H_{18}O_4$	63.65	8.02
22	72.9	120–122	92.8	7.2	64.79	8.25	$C_{13}H_{20}O_4$	64.98	8.39
23	69.0	110–113	92.8	7.2	64.88	8.28	$C_{13}H_{20}O_4$	64.98	8.39
24	61.5	132–135	94.2	7.6	66.04	8.49	$C_{14}H_{22}O_4$	66.14	8.61
25	90.1	78–80	93.3	6.7	62.11	7.49	$C_{11}H_{16}O_4$	62.24	7.59
26	85.4	89–91	93.1	6.9	63.48	8.00	$C_{12}H_{18}O_4$	63.65	8.02
27	76.0	114–116	92.8	7.2	64.79	8.28	$C_{13}H_{20}O_4$	64.98	8.39
28	72.5	129–131	92.6	7.8	66.03	8.41	$C_{14}H_{22}O_4$	66.14	8.61
29	64.0	121–123	92.4	7.6	66.02	8.52	$C_{14}H_{22}O_4$	66.14	8.61
30	60.9	144–146	92.1	7.9	67.04	9.00	$C_{15}H_{24}O_4$	67.14	9.01
31	87.0	76–79	92.9	7.1	62.11	7.47	$C_{11}H_{16}O_4$	62.24	7.59
32	84.5	87–90	92.8	7.2	63.49	8.00	$C_{12}H_{18}O_4$	63.65	8.02
33	82.0	110–114	92.5	7.5	64.85	8.18	$C_{13}H_{20}O_4$	64.98	8.39
34	78.3	128–130	92.2	7.8	64.03	8.51	$C_{14}H_{22}O_4$	66.14	8.61
35	72.8	118–120	92.2	7.8	66.01	8.60	$C_{14}H_{22}O_4$	66.14	8.61
36	69.0	140–142	92.0	8.0	67.05	8.99	$C_{15}H_{24}O_4$	67.14	9.01
37	82.0	84–85	93.2	6.8	63.11	8.00	$C_{12}H_{18}O_4$	63.69	8.08
38	78.1	97–98	92.6	7.4	64.81	8.21	$C_{13}H_{20}O_4$	64.97	8.39
39	75.4	119–120	92.2	7.8	66.00	8.53	$C_{14}H_{22}O_4$	66.11	8.71
40	71.6	135–137	91.4	8.6	67.03	10.52	$C_{15}H_{24}O_4$	67.67	9.02
41	68.0	121–122	91.4	8.6	67.01	10.50	$C_{15}H_{24}O_4$	67.67	9.02
42	61.5	149–150	90.7	9.3	68.03	9.07	$C_{16}H_{26}O_4$	68.57	9.28

Scheme 1.



R = H (**7**, **13**, **19**, **25**, **31**, **37**, **42**), CH_3 (**3**, **8**, **14**, **20**, **26**, **32**, **38**), CH_3CH_2 (**4**, **9**, **15**, **21**, **27**, **33**, **39**), $CH_3(CH_2)_2$ (**10**, **16**, **22**, **28**, **34**, **40**), $(CH_3)_2CH$ (**11**, **17**, **23**, **29**, **35**, **41**), $CH_3(CH_2)_3$ (**12**, **18**, **24**, **30**, **36**, **42**); R^1 = H (**3**, **4**, **19**–**30**), CH_3 (**5**, **6**, **31**–**42**).

Scheme 2.



The synthesized diesters are colorless liquids having a pleasant, characteristic odor, which makes them good candidates for aromatizer applications. For example, 5-acetoxybicyclo[2.2.1]hept-2-yl acetate **8** was tested at the Ekotest laboratory, certified for quality assessment of cosmetics and detergents (AZS İSO/İEC170252009 Standard), and recommended for use in detergent formulations.

EXPERIMENTAL

The composition and purity of the synthesized diesters were determined by GLC on an LKhM-8MD chromatograph in the following conditions: column 1.5 m packed with 10 wt % poly(ethylene succinate) on Spherochrom, injector temperature 250°C, oven temperature 180°C, detector temperature

120°C, carrier gas (helium) flow rate 60 mL/min. The IR spectra were measured on a UR-20 spectrophotometer. The NMR spectra were run on a Bruker AV-300 spectrometer and 300 (^{1}H) and 75 MHz (^{13}C) in acetone-d_6.

(Bicyclo[2.2.1]hept-2-ene-5-yl) acetate (1) [99.8%, bp 60–61°C (10 mmHg), d_4^{20} 1.070 g/mL, n_D^{20} 1.4570] and (bicyclo[2.2.1]hept-2-ene-5-yl)methyl acetate (**2**) [99.8%, bp 78–79°C (10 mmHg), d_4^{20} 1.0558 g/mL, n_D^{20} 1.4768] were synthesized by the [4+2]-cycloaddition of cyclopentadiene to vinyl acetate and allyl acetate, respectively [7, 8]. Methyl bicyclo[2.2.1]hept-2-ene-5-carboxylate (**3**) [bp 78–79°C (17 mmHg), d_4^{20} 1.0516 g/mL, n_D^{20} 1.4761], methyl 5-methyl-bicyclo[2.2.1]hept-2-ene-5-carboxylate (**4**) [bp 105–106°C (17 mmHg), d_4^{20} 1.0309 g/mL, n_D^{20} 1.4712], ethyl bicyclo[2.2.1]hept-2-ene-5-carboxylate (**5**) [bp 90–91°C (17 mmHg), d_4^{20} 1.0208 g/mL, v 1.4686], and ethyl 5-methylbicyclo-[2.2.1]hept-2-ene-5-carboxylate (**6**) [bp 112–113°C (17 mmHg), d_4^{20} 1.0361 g/mL, n_D^{20} 1.4785] were synthesized by the condensation of cyclopenta-diene with methyl and ethyl acrylate and methacrylate in the presence of a nano-TiO_2 catalyst (20–22 nm) be the procedures in [9, 10]. According to the GLC data, unsaturated bicyclic monoesters **1–6** were mixtures of the *exo* and *endo* isomers (55–60 and 40–45%, respectively). According to [11], on heating, the *endo* isomers transform into thermodynamically more stable e*xo* isomers. Therefore, we heated the resulting isomer mixtures to obtain the *exo* isomer (by GLC, 99.0%).

5-Acetoxybicyclo[2.2.1]hept-2-yl acetate (8). A mixture of 152 g of compound **1,** 100 g of acetic acid, and 0.1 g of $BF_3{\cdot}OEt_2$ was heated at 80°C for 3 h. Vacuum distillation gave 175.7 g (87%) of compound **8**. IR spectrum, ν, cm^{-1}: 1200–1210 (C–O–C), 1380 (CH_3), 1460 (CH_2), 1730 (C=O), 3000 (CH). ^{1}H NMR spectrum, δ, ppm: 1.70–1.90 m (6H, 3CH_2), 2.21–2.35 s (6H, 2CH_3), 2.40–2.60 m (2H, 2CH), 4.10–4.20 m (2H, 2CH), ^{13}C NMR spectrum, δ_C, ppm: 19.0 (C^{11}), 21.0 (C^{10}), 29.0 (C^7), 35.0 (C^6), 38.0 (C^3), 44.0 (C^4), 48.0 (C^1), 78.5 (C^2), 79.0 (C^5), 169.3 (C^9), 170.2 (C^8).

5-(Acetoxymethyl)bicyclo[2.2.1]hept-2-yl acetate (14) was prepared in a similar way. Yield 191 g (84.5%). IR spectrum, ν, cm^{-1}: 2800 (CH), 1740 (C=O), 1200–1230 (C–O–C), 1460 (CH_2), 1380 (CH_3). ^{1}H NMR spectrum, δ, ppm: 1.60–2.00 m (6H, 3CH_2), 2.20 d (6H, 2CH_3, J = 8.0 Hz), 2.60 d (2H, 2CH, J = 8.3 Hz), 4.2 m (1H, CH), 4.8 d (1H, CH, J = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 20.7 (C^{11}), 21.1 (C^{12}), 28.4 (C^6), 30.4 (C^7), 37.5 (C^4), 39.3 (C^5), 39.4 (C^3), 41.9 (C^1), 64.8 (C^9), 76.8 (C^2), 170.2 (C^8), 170.2 (C^{10}).

5-(Methoxycarbonyl)bicyclo[2.2.1]hept-2-yl formate (19) was prepared in a similar way. Yield 92%. IR spectrum, ν, cm^{-1}: 2885 (CH), 1735 (C=O), 1200–1240 (C–O–C), 1460 (CH_2), 1380 (CH_3). ^{1}H NMR spectrum, δ, ppm: 1.63–1.95 m (6H, 3CH_2), 2.07–2.54 m (2H, 2CH), 2.26 m (1H, CH), 3.68 s (3H, CH_3), 3.90 d (1H, CH, J = 7.5 Hz), 8.04 s (1H, HCOO, J = 8.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.2 (C^7), 30.1 (C^3), 32.3 (C^6), 36.1 (C^4), 38.4 (C^1), 46.2 (C^5), 50.5 (C^{10}), 81.3 (C^2), 158.0 (C^8), 175.8 (C^9).

5-(Methoxycarbonyl)bicyclo[2.2.1]hept-2-yl acetate (20) was prepared in a similar way. Yield 88%. IR spectrum, ν, cm^{-1}: 2800 (CH), 1740 (C=O), 1200–1250 (C–O–C), 1460 (CH_2), 1380 (CH_3). ^{1}H NMR spectrum, δ, ppm: 1.63–1.95 m (6H, 3CH_2), 2.07–2.54 m (2H, 2CH), 2.21 d (3H, CH_3, J = 8.3 Hz), 2.26 m (1H, CH), 3.68 s (3H, CH_3), 3.90 d (1 H, CH, J = 8.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 170.2 (C^8), 175.8 (C^9), 76.5 (C^2), 46.2 (C^5), 38.3 (C^1), 36.2 (C^4), 32.3 (C^6), 37.2 (C^3), 28.2 (C^7), 50.4 (C^{10}), 21.6 (C^{12}).

5-Methyl-5-(methoxycarbonyl)bicyclo[2.2.1]hept-2-yl formate (25) was prepared in a similar way. Yield 87%. IR spectrum, ν, cm^{-1}: 1200–1250 (C–O–C), 1380 (CH_3), 1460 (CH_2), 1730–1740 (C=O), 3000–2800 (CH). ^{1}H NMR spectrum, δ, ppm: 1.38 m (3H, CH_3), 1.63–1.95 m (6H, 3CH_2), 2.26 m (1H, CH), 3.68 s (3H, CH_3), 3.90 d (1 H, CH, J = 8.3 Hz), 8.04 d (1H, HCOO, J = 8.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 27.4 (C^{13}), 30.9 (C^7), 33.3 (C^6), 34.4 (C^3), 38.6 (C^1), 46.1 (C^5), 46.2 (C^4), 52.5 (C^{10}), 81.6 (C^2), 160.7 (C^8), 177.8 (C^9).

5-Ethyl-5-(methoxycarbonyl)bicyclo[2.2.1]hept-2-yl formate (31) was prepared in a similar way. Yield 82%. IR spectrum, ν, cm^{-1}: 1200–1250 (C=O), 1380 (CH_3), 1460 (CH_2), 1730–1740 (C=O), 3000–2800 (CH). ^{1}H NMR spectrum, δ, ppm: 1.29 m (3H, CH_3), 1.63–1.95 m (6H, 3CH_2), 2.07–2.54 m (2H, 2CH), 2.26 m (1H, CH), 3.90 d (1H, CH, J = 7.5 Hz), 4.21 t (2H, CH_2, J = 8.5 Hz), 8.04 d (1H, HCOO, J = 8.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.1 (C^{11}), 27.4 (C^{13}), 30.9 (C^7), 33.2 (C^6), 34.4 (C^3), 38.4 (C^1), 46.1 (C^5), 46.2 (C^4), 61.9 (C^{10}), 81.6 (C^2), 160.7 (C^8), 177.8 (C^9).

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