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Synthesis of Esters from Cage-Like Unsaturated Hydrocarbons, Carboxylic Acid Anhydrides, and Water

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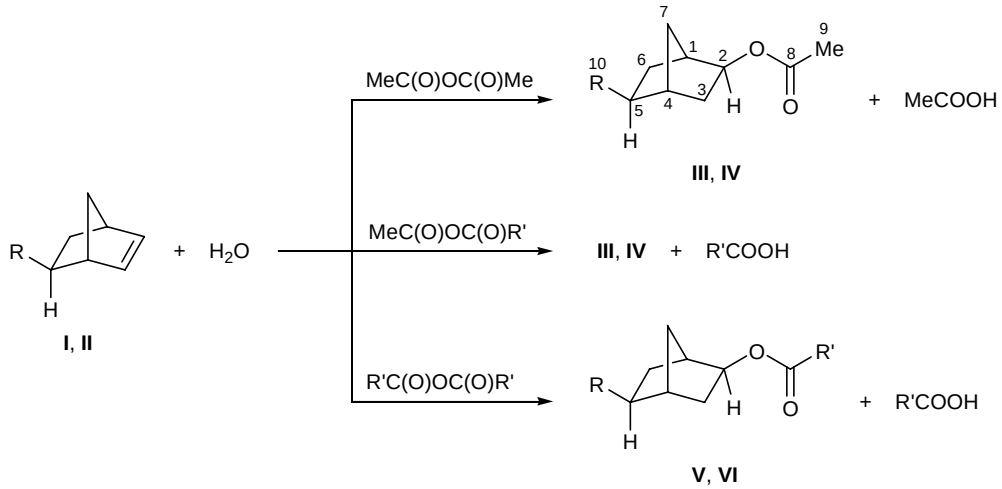
Abstract—A convenient method for the preparation of esters was developed on the basis of reaction of cage-like polycyclic olefins with carboxylic acid anhydrides and water. Mixed anhydrides were found to give rise to the corresponding low-molecular acid esters. Among the obtained esters, acetates possess a pleasant odor, and they can be used as components of synthetic fragrant substances.

Alicyclic esters derived from saturated monocarboxylic acids are successfully used in perfumery as components of synthetic fragrant substances [1, 2]. These compounds are starting materials in the synthesis of bicyclic ketones, such as camphor and norcamphor, which are used in medicine as antiseptics and for the preparation of smokeless powder [3]. Bornyl isovalerate and myrtenyl isovalerate are known as sedative agents for treatment of nervous excitements and cardiovascular neuroses accompanied by coronary vasospasms and tachycardia [4]; these esters are also used in the preparation of printer's inks [5].

We previously developed procedures for the synthesis of alicyclic esters by catalytic and thermal addition of monocarboxylic acids to cyclic olefins [6, 7] and of diesters by acylation and acetoxylation of unsaturated bicyclic alcohols [8]. The present communication reports on the synthesis of esters under mild conditions by reactions of cyclic olefins with saturated monocarboxylic acid anhydrides and water. Cage-like cyclic olefins, bicyclo[2.2.1]hept-2-ene (**I**) and its 5-methyl-substituted analog **II** reacted with water and acetic, propionic, and mixed acetic propionic anhydrides at a ratio of 1:1:1 (140–160°C, reaction time 4 h) to give the corresponding bicyclic esters **III**–**VI** in 72–94% yield (Scheme 1). According to the GLC data, bicyclo[2.2.1]hept-2-ene (**I**) gave rise to stereoisomerically pure bicyclo[2.2.1]hept-*exo*-2-yl acetate (**III**), while from *exo*-5-methylbicyclo[2.2.1]-hept-2-ene (**II**) we obtained a mixture of two regio-

Scheme 1.



I, **III**, **V**, R = H; **II**, **IV**, **VI**, R = Me; R' = Et.

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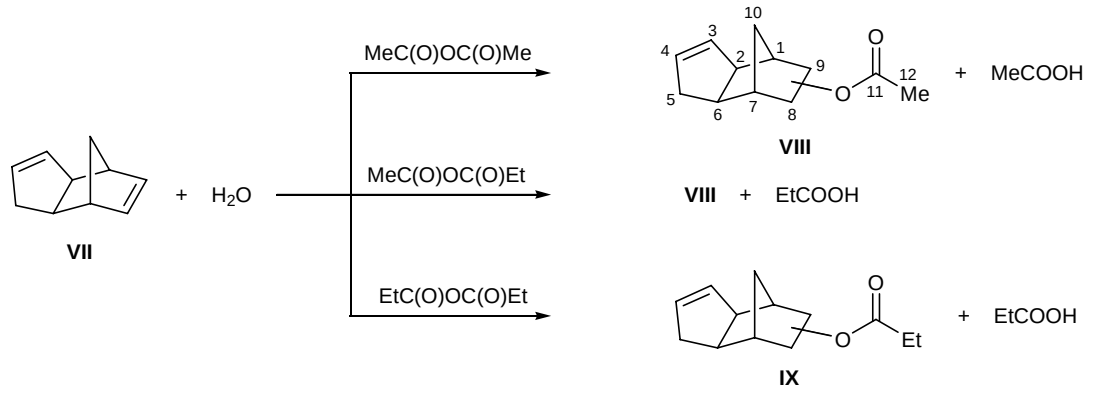
Scheme 2.



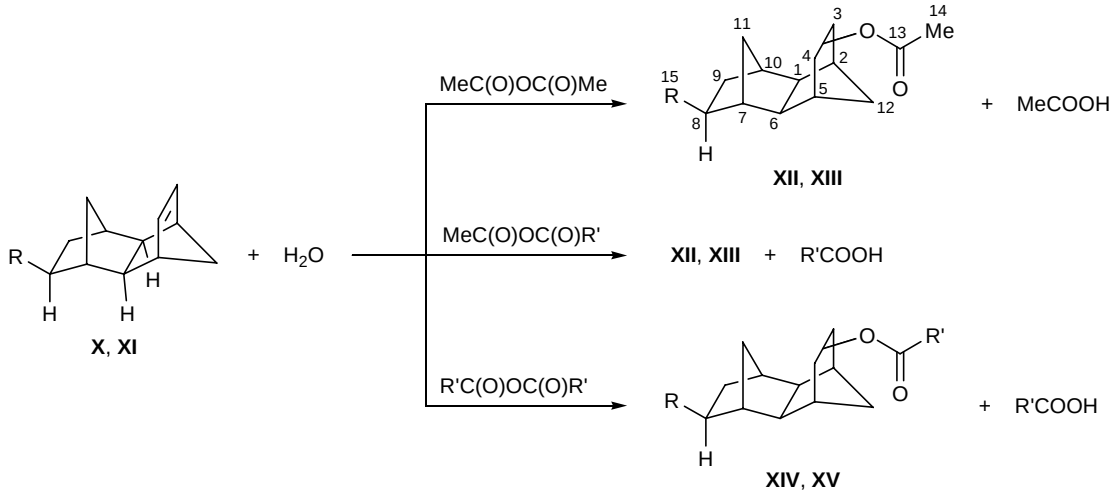
isomers: 97.0% of *exo*-5-methylbicyclo[2.2.1]hept-*exo*-2-yl acetate (**IV**) and 3.0% of *exo*-6-methylbicyclo[2.2.1]hept-*exo*-2-yl acetate.

The reaction of **I** and **II** with acetic propionic anhydride at 150°C afforded only the corresponding acetates **III** and **IV** in 83–85% yield. Here, the regioselectivity was higher than in the reaction with acetic anhydride. From 5-methylbicyclo[2.2.1]hept-2-ene, acetic propionic anhydride, and water we obtained 99.5% of *exo*-5-methylbicyclo[2.2.1]hept-*exo*-2-yl acetate (**IV**), while the fraction of the *exo*-6-methyl isomer was as small as 0.5%. The reactions of bicyclic olefins **I** and **II** with propionic anhydride required a higher temperature (by 10°C), as compared to acetic propionic anhydride. The products were propionic acid esters **V** and **VI** which were formed in 72–77% yield.

In order to elucidate how the nature of the cage-like skeleton affects the process, we examined analogous reactions of *exo*-tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**VII**). The reactions of **VII** with acetic, acetic propionic, and propionic anhydrides involved the double bond in the norbornene fragment, and the products were tricyclo[5.2.1.$0^{2,6}$]dec-3-en-8(9)-yl esters **VIII** and **IX** (yield 72–91%; Scheme 2). Likewise, *exo*,*exo*-tetracyclo[4.4.$1^{2,5}$.$1^{7,10}$.$0^{1,6}$]dodec-3-ene (**X**) and its 8-methyl-substituted analog **XI** reacted with the same anhydrides in the presence of water to afford the corresponding tetracyclic esters **XII**–**XV** in 61–85% yield (Scheme 3).

The structure of the products was additionally confirmed by independent syntheses, i.e., by acylation of the corresponding alcohols according to the procedure described in [9]. The purity of the isolated products was 99.7–99.9%. In the IR spectra of these compounds we observed strong absorption bands in the regions 1730–1740 and 1200–1250 cm^{-1}, which are typical of ester groups. Their ^{1}H NMR spectra contained signals at δ 4.60–4.80 ppm due to *exo*-protons. The ester

Scheme 3.



X, **XII**, **XIV**, R = H; **XI**, **XIII**, **XV**, R = Me; R' = Et.

carbonyl carbon atoms give signals at δ_C 160.98–169.7 ppm in the ^{13}C NMR spectra.

The esters were isolated as colorless transparent liquids possessing a grass, flower, or fruit odor, and they may be recommended for use as components of fragrant substances.

EXPERIMENTAL

The IR spectra were recorded on a UR 20 instrument. The ^1H NMR spectra were measured on a Tesla BS-487 instrument (80 MHz) using carbon tetrachloride as solvent and hexamethyldisiloxane as internal reference. The ^{13}C NMR spectra were obtained on a Varian spectrometer at 80 MHz from solutions in dioxane. The initial compound and reaction products were analyzed by GLC on an LKhM-8MD chromatograph (1.5-m column, stationary phase 10% of polyethylene glycol succinate on Sferokhrom; injector temperature 200–250°C, oven temperature 120–150°C; carrier gas helium, flow rate 45 ml/min)..

Initial cyclic olefins, bicyclo[2.2.1]hept-2-ene (**I**) and 5-methylbicyclo[2.2.1]hept-2-ene (**II**), were synthesized by Diels–Alder reaction of cyclopentadiene with ethylene and propylene, respectively; tetracyclo[$4.4.1^{2,5}.1^{7,10}.0^{1,6}$]dodec-3-ene (**X**) and 8-methyltetracyclo[$4.4.1^{2,5}.1^{7,10}.0^{1,6}$]dodec-3-ene (**XI**) were prepared by the procedures reported in [10, 11]. The initial cyclic olefins were preliminarily converted into *exo* isomers by treatment with $AlCl_3$ in methylene chloride according to [12]: *exo*-5-methylbicyclo[2.2.1]hept-2-ene (**II**), bp 116°C, d_4^{20} = 0.8602, n_D^{20} = 1.4599; *exo*-tricyclo[$5.2.1.0^{2,6}$]deca-3,8-diene (**VII**), mp 19.5°C; *exo,exo*-tetracyclo[$4.4.1^{2,5}.1^{7,10}.0^{1,6}$]dodec-3-ene (**X**), bp 94–95°C (11 mm), d_4^{20} = 1.0002, n_D^{20} = 1.5168; *exo,exo*-8-methyltetracyclo[$4.4.1^{2,5}.1^{7,10}.0^{1,6}$]dodec-3-ene (**XI**), bp 128–129°C (28 mm), d_4^{20} = 1.0012, n_D^{20} = 1.5190.

The reactions were performed in a stainless steel high-pressure reactor.

Bicyclo[2.2.1]hept-*exo*-2-yl acetate (III). *a*. A mixture of 27 g of compound **I**, 51 g of acetic anhydride, and 9 g of water was heated for 4 h at 140°C. Acetic acid was distilled off, and fractional distillation under reduced pressure gave 72 g (94%) of compound **III** with bp 100–101°C (30 mm), d_4^{20} = 1.0268, n_D^{20} = 1.4565. IR spectrum, ν, cm^{-1}: 1730 (C=O), 1220 (C–O–C), 1380 (CH_3). ^1H NMR spectrum, δ, ppm: 1.30–1.90 d (8H, CH_2), 2.20 s (3H, CH_3), 2.50–2.55 m (2H, CH), 4.75 d (2H, CH). ^{13}C NMR spectrum, δ_C, ppm: 20.94 (CO**C**H_3), 24.74 (C^6), 28.62 (C^5), 35.57 (C^7), 35.92 (C^4), 40.04 (C^3), 41.98 (C^1), 77.42 (C^2), 169.7 (CO). Found, %: C 70.05; H 9.10. $C_9H_{14}O_2$. Calculated, %: C 70.08; H 9.14.

b. Ester **III** was synthesized in a similar way from 47 g of compound **I**, 58 g of acetic propionic anhydride, and 9 g of water; the mixture was stirred for 4 h at 150°C. Yield 63.4 g (83%), bp 100–102°C (30 mm), d_4^{20} = 1.0302, n_D^{20} = 1.4588.

***exo*-5-Methylbicyclo[2.2.1]hept-*exo*-2-yl acetate (IV).** *a*. A mixture of 54 g of compound **II**, 51 g of acetic anhydride, and 9 g of water was heated for 4 h at 140°C. Acetic acid was distilled off, and fractional distillation under reduced pressure gave 75.6 g (90%) of ester **IV** with bp 106–107°C (30 mm), d_4^{20} = 1.0035, n_D^{20} = 1.4612. IR spectrum, ν, cm^{-1}: 1730 (C=O), 1220 (C–O–C), 1380 (CH_3), 1375 (CH_3). ^1H NMR spectrum, δ, ppm: 1.24 s (3H, CH_3), 1.30–1.90 d (8H, CH_2), 2.20 s (3H, CH_3), 2.24 s (3H, CH_3), 2.45 m (2H, CH), 4.75 d (2H, CH). ^{13}C NMR spectrum, δ_C, ppm: 17.10 (CH_3), 20.95 ($COCH_3$), 32.62 (C^5), 33.44 (C^6), 37.10 (C^7), 37.44 (C^4), 39.64 (C^3), 42.42 (C^1), 74.22 (C^2), 166.36 (CO). Found, %: C 71.38; H 9.49. $C_{10}H_{16}O_2$. Calculated, %: C 71.42; H 9.52.

b. Likewise, from 54 g of compound **II**, 58 g of acetic propionic anhydride, and 9 g of water (150°C, 4 h) we obtained 71.4 g (85%) of ester **IV**, bp 106–107°C (30 mm), d_4^{20} = 1.0045, n_D^{20} = 1.4622.

Bicyclo[2.2.1]hept-*exo*-2-yl propionate (V). A mixture of 47 g of compound **I**, 65 g of propionic anhydride, and 9 g of water was heated for 4 h at 160°C. Vacuum fractionation gave 63.7 g (76.6%) of ester **V**, bp 100–101°C (25 mm), d_4^{20} = 0.9998, n_D^{20} = 1.4592. IR spectrum, ν, cm^{-1}: 1730 (C=O), 1220 (C–O–C), 1380 (CH_3). Found, %: C 71.10; H 9.32. $C_{10}H_{16}O_2$. Calculated, %: C 71.42; H 9.52.

***exo*-5-Methylbicyclo[2.2.1]hept-exo-2-yl propionate (VI).** A mixture of 54 g of compound **II**, 65 g of propionic anhydride, and 9 g of water was heated for 4 h at 160°C. Yield 65.5 g (72%), bp 119–120°C (4 mm), d_4^{20} = 0.9891, n_D^{20} = 1.4616. IR spectrum, ν, cm^{-1}: 1730 (C=O), 1220 (C–O–C), 1380 (CH_3), 1375 (CH_3). Found, %: C 72.39; H 9.70. $C_{11}H_{18}O_2$. Calculated, %: C 72.53; H 9.89.

***exo*-Tricyclo[$5.2.1.0^{2,6}$]dec-3-en-*exo*-8(9)-yl acetate (VIII).** *a*. A mixture of 66 g of compound **VII**, 51 g of acetic anhydride, and 9 g of water was heated for 4 h at 140°C. Yield 87 g (90.6%), bp 130–131°C (10 mm), d_4^{20} = 1.0620, n_D^{20} = 1.5038. IR spectrum, ν, cm^{-1}: 1730 (C=O), 1220 (C–O–C), 1380 (CH_3). ^1H NMR spectrum, δ, ppm: 1.36 m (2H, CH_2), 2.00 d (2H, CH), 2.26 m (4H, CH_2), 2.52–2.62 m (2H, CH),

4.81–4.88 d (2H, CH), 5.75–5.90 q (2H, CH=). ^{13}C NMR spectrum, δ_C, ppm: 17.62 ($COCH_3$), 26.00 (C^{10}), 35.53 (C^5), 36.02 (C^9), 37.88 (C^7), 38.93 (C^1), 41.92 (C^6), 45.72 (C^2), 73.90 (C^8), 121.69 (C^3), 128.55 (C^4), 166.2 (CO). Found, %: C 74.62; H 8.26. $C_{12}H_{16}O_2$. Calculated, %: C 74.91; H 8.35.

b. A mixture of 66 g of compound **VII**, 58 g of acetic propionic anhydride, and 9 g of water was heated for 4 h at 150°C. Yield 78.2 g (81.5%), bp 130–132°C (10 mm), d_4^{20} = 1.0602, n_D^{20} = 1.5033.

***exo*-Tricyclo[5.2.1.0^{2,6}]dec-3-en-*exo*-8(9)-yl propionate (IX).** A mixture of 66 g of compound **VII**, 65 g of propionic anhydride, and 9 g of water was heated for 4 h at 160°C. Yield 73.7 g (71.6%), bp 108–110°C (2 mm), d_4^{20} = 1.0546, n_D^{20} = 1.5059. IR spectrum, ν, cm^{-1}: 1730 (C=O), 1220 (C–O–C), 1380 (CH_3). Found, %: C 75.42; H 8.50. $C_{13}H_{18}O_2$. Calculated, %: C 75.67; H 8.78.

***exo,exo*-Tetracyclo[4.4.1^{2,5}.1^{7,10}.0^{1,6}]dodec-*exo*-3-yl acetate (XII).** *a*. A mixture of 80 g of compound **X**, 51 g of acetic anhydride, and 9 g of water was heated for 4 h at 140°C. Yield 93 g (84.6%), bp 155–156°C (10 mm), d_4^{20} = 1.0963, n_D^{20} = 1.5060. IR spectrum, ν, cm^{-1}: 1730 (C=O), 1220 (C–O–C), 1380 (CH_3). ^{1}H NMR spectrum, δ, ppm: 1.75–1.81 m (4H, CH_2), 2.15 s (3H, CH_3), 2.11–2.35 m (2H, CH), 2.41–2.65 d (2H, CH), 4.78 m (1H, CH). ^{13}C NMR spectrum, δ_C, ppm: 14.48 ($COCH_3$), 24.93 (C^9), 28.51 (C^8), 29.52 (C^{11}), 32.71 (C^{12}), 33.85 (C^{10}), 33.93 (C^7), 34.04 (C^6), 35.09 (C^1), 40.30 (C^5), 42.62 (C^4), 42.87 (C^2), 70.96 (C^3), 162.72 (CO). Found, %: C 76.20; H 9.11. $C_{14}H_{20}O_2$. Calculated, %: C 76.32; H 9.14.

b. Ester **XII** was obtained from 80 g of compound **X**, 58 g of acetic propionic anhydride, and 9 g of water (150°C, 4 h). Yield 86 g (78.5%), bp 155–156°C (10 mm), d_4^{20} = 1.0972, n_D^{20} = 1.5041.

***exo,exo*-8-Methyltetracyclo[4.4.1^{2,5}.1^{7,10}.0^{1,6}]-dodec-*exo*-3(4)-yl acetate (XIII).** *a*. A mixture of 87 g of compound **XI**, 51 g of acetic anhydride, and 9 g of water was heated for 4 h at 140°C. Yield 80 g (68.5%), bp 190–192°C (10 mm), d_4^{20} = 1.0651, n_D^{20} = 1.5156. IR spectrum, ν, cm^{-1}: 1730 (C=O), 1220 (C–O–C), 1380 (CH_3), 1375 (CH_3). ^{1}H NMR spectrum, δ, ppm: 1.28 s (3H, CH_3), 1.78–1.95 m (2H, CH), 2.15 s (3H, CH_3), 2.21 m (2H, CH_2), 2.40–2.65 m (2H, CH), 2.55–2.62 m (2H, CH), 3.80 d (1H, CH), 4.80 d (1H, CH). ^{13}C NMR spectrum, δ_C, ppm: 13.81 (CH_3), 14.42 ($COCH_3$), 24.91 (C^9), 28.51 (C^8), 29.52 (C^{11}), 32.70 (C^{12}), 33.80 (C^{10}), 33.90 (C^7), 34.04 (C^6), 35.08 (C^1), 40.62 (C^4), 42.31 (C^5), 42.85 (C^2), 70.95 (C^3), 161.98 (CO). Found, %: C 78.74; H 9.40. $C_{15}H_{22}O_2$. Calculated, %: C 78.88; H 9.45.

b. A mixture of 87 g of compound **XI**, 58 g of acetic propionic anhydride, and 9 g of water was heated for 4 h at 150°C. Yield 73 g (62.3%), bp 151–153°C (2 mm), d_4^{20} = 1.0111, n_D^{20} = 1.5200.

***exo,exo*-Tetracyclo[4.4.1^{2,5}.1^{7,10}.0^{1,6}]dodec-*exo*-3-yl propionate (XIV).** A mixture of 80 g of compound **X**, 65 g of propionic anhydride, and 9 g of water was heated for 4 h at 160°C. Yield 82 g (70%), bp 132–136°C (2 mm), d_4^{20} = 1.0708, n_D^{20} = 1.5168. IR spectrum, ν, cm^{-1}: 1730 (C=O), 1220 (C–O–C), 1380 (CH_3). Found, %: C 78.71; H 9.31. $C_{15}H_{22}O_2$. Calculated, %: C 78.88; H 9.45.

***exo,exo*-8-Methyltetracyclo[4.4.1^{2,5}.1^{7,10}.0^{1,6}]-dodec-*exo*-3(4)-yl propionate (XV).** A mixture of 87 g of compound **XI**, 65 g of propionic anhydride, and 9 g of water was heated for 4 h at 160°C. Yield 75 g (60%), bp 150–152°C (2 mm), d_4^{20} = 1.0109, n_D^{20} = 1.52018. IR spectrum, ν, cm^{-1}: 1730 (C=O), 1220 (C–O–C), 1380 (CH_3), 1375 (CH_3). Found, %: C 77.18; H 9.60. $C_{16}H_{24}O_2$. Calculated, %: C 77.42; H 9.67.

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