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Synthesis of 8-Acetoxytetracyclo[4.4.1$^{2.5}$.1$^{7.10}$.0$^{1.6}$]dodec-3-ene and Diesters of C_1–C_5 Acids on Its Basis

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Abstract—Reaction of vinyl acetate with tricyclo[5.2.1$^{2.5}$.1.0$^{2.6}$]deca-3,8-diene in the presence of nano-TiO_2 (20 nm) catalyst was studied. 8-Acetoxytetracyclo[4.4.1$^{2.5}$.1$^{7.10}$.0$^{1.6}$]dodec-3-ene was obtained in 88.5% yield. Addition of saturated monobasic acids C_1–C_5 to the obtained unsaturated monoester in the presence of the boron trifluoride etherate catalyst was investigated. Corresponding diesters were obtained in 68.1–93.0% yield. They can be used as the additives to synthetic oils and as components of perfumes.

Keywords: nano-TiO_2, dicyclopentadiene, condensation, vinyl acetate, tetracyclododecene, boron trifluoride etherate

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Diesters of polycyclic diols and hydroxy acids are known to be successfully used as the plasticizers of polymer materials significantly improving the physicochemical properties [1].

Diesters of saturated asids are also used to improve the quality of mineral oils and their operating properties [2].

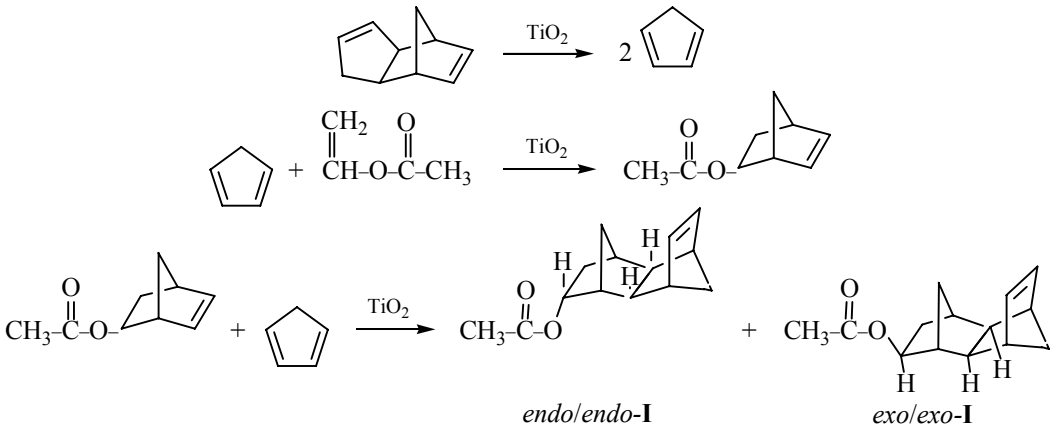
Diesters of polycyclic diols are utilized in the perfumery as components of synthetic aromatic substances as reported in scientific publications [3–5].

Recently we have studied cycloaddition of cyclopentadiene with vinyl acetate affording and 5-acetoxybicyclo[2.2.1]hept-2-ene [6]. In this work it was also shown that besides monoadduct insignificant amount of bis-adduct, 8-acetoxytetracyclo[4.4.1$^{2.5}$.1$^{7.10}$.0$^{1.6}$]dodec-3-ene **I** formed.

In this study with the purpose of the synthesis of new diesters of tetracyclododecanediol we have studied the reaction of vinyl acetate with tricyclo [5.2.1.0$^{2.6}$]-deca-3,8-diene.

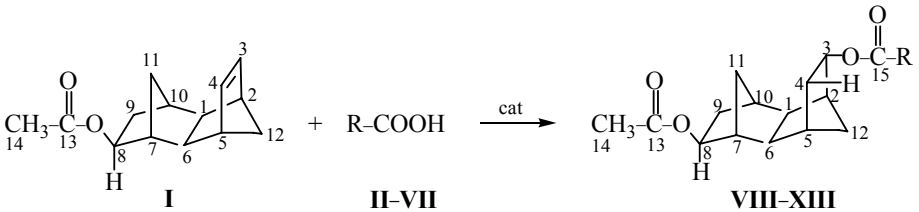
The depolymerization of tricyclo[5.2.1.0$^{2.6}$]deca-3,8-diene to cyclopentadiene and its condensation with vinyl acetate was carried out in the presence of heterogenic nano-TiO_2 catalyst (20 nm) (Scheme 1).

Scheme 1.



endo/*endo*-**I** *exo*/*exo*-**I**

Scheme 2.



I **II–VII** **VIII–XIII**

R = H (**II**), CH_3 (**III**), CH_3CH_2 (**IV**), $(CH_3)_2CH$ (**V**), $CH_3(CH_2)_2$ (**VI**), C_4H_9 (**VII**).

All three stages of the reaction simultaneously proceed in a pressure reactor. The effect of temperature, of molar ratio of components, of the reaction time, and of the amount of nano-TiO_2 catalyst on the yield of compound **I** was studied, and optimal parameters of synthetic procedure for the target product were evaluated. It was shown that optimum parameters of synthesis areas follows: tricyclo[5.2.1.0$^{2.6}$]deca-3,8-diene : vinyl acetate molar ratio 1 : 1–1.25 wt % of nano-TiO_2 catalyst, 0.2 mass % of hydroquinone with respect to tricyclo[5.2.1.0$^{2.6}$]deca-3,8-diene, temperature 190°C, and the reaction time 4 h. After filtering of the heterogenic catalyst and distillation in a vacuum the target product **I** was obtained in 88.5% yield.

The composition and purity of the synthesized unsaturated tetracyclic monoesters were evaluated by means of GLC. It was shown that monoester is a mixture of 28.0% of *endo-endo*- and 72% of *exo-exo*-steric isomers.

The product obtained was heated at 200°C for 1 h to carry out isomerization of the mixture to most stable *exo-exo*-isomer [7]. This process resulted in the formation of monoester containing 99.9% of *exo-exo*- and 0.1% of *endo-endo*- isomer.

In the second step of our work the synthesis of diesters by catalytic addition of saturated C_1-C_5 monobasic acids to cycloalkene **I** was investigated. Boron trifluoride etherate as catalyst was used. The reaction can be described by the Scheme 2.

By an example of acetic acid the effect of temperature, of molar ratio of the reaction components, of the amount of catalyst, and of the reaction time on the yield of tetracyclo[4.4.1$^{2.5}$.1$^{7.10}$.0$^{1.6}$]dodecan-3.8-diol diacetate **IX** was studied.

I : III molar ratio 1 : 1, 0.2 wt % of catalyst and the reaction time 3 h were used as starting conditions. The temperature of the reaction was varied with in the limits 70–120°C. At the increase in temperature from 70 to 90°C the yield of tetracyclododecan-3,8-diol diacetate **IX** increases from 52.5 to 70.0%. Further increase in temperature to 120°C causes the decrease in the yield of compound **IX** to 50.0% due to the formation of side products of dimerization and oligomerization of the starting substance **I**. Therefore 90°C was accepted as the optimum reaction temperature (see Fig. 1a).

The dependence of the target product yield on the **I : III** reagent ratio was studied in the range 1 : (1–1.5) (see Fig. 1b). Experiments were carried out at 90°C for 3 h using 0.2 wt % of catalyst. The yield of diester **IX** grows from 45.5 to 76.0% at the increase of reagent ratio from 1 : 1 to 1 : 1.3. Further increase to 1.5 mol decreases the yield of the target product to 73.2%.

The influence of the catalyst amount was studied at the above-established optimum values of the temperature and reagent ratio and the reaction time 3 h (see Fig. 1c). Amount of catalyst was varied in the range 0.4–0.6 wt %. The use of 0.5 wt % of catalyst was optimal, because the yield increased from 60% to 79%. Using larger amount of the boron trifluoride etherate decreased the target product yield to 56.5%.

Yield of compound **IX** depends also significantly on the reaction time (see Fig. 1d). Its increase from 1 to 4 h permits to achieve 90% yield of diacetate, but more prolonged heating decreases the yield of compound **IX** to 85%.

Hence, optimal parameters of diacetate **IX** formation in the reaction of compound **I** with the acetic acid **III** in the presence of boron trifluoride etherate are as follows: reaction temperature 90°C, molar ratio of compounds **I** and **III 1 :** 1.3**,** amount of the catalyst 0.5 wt % with respect to substance **I**, reaction time 4 h. Under optimum conditions yield of product **IX** reaches 90%. Addition of formic **II,** propionic **IV,** butyric **V,** isobutyric **VI,** and *n*-valeric **VII** acids was carried out analogously. Yields of the products, their physicochemical characteristic, and elemental analysis data are listed in Table 1.

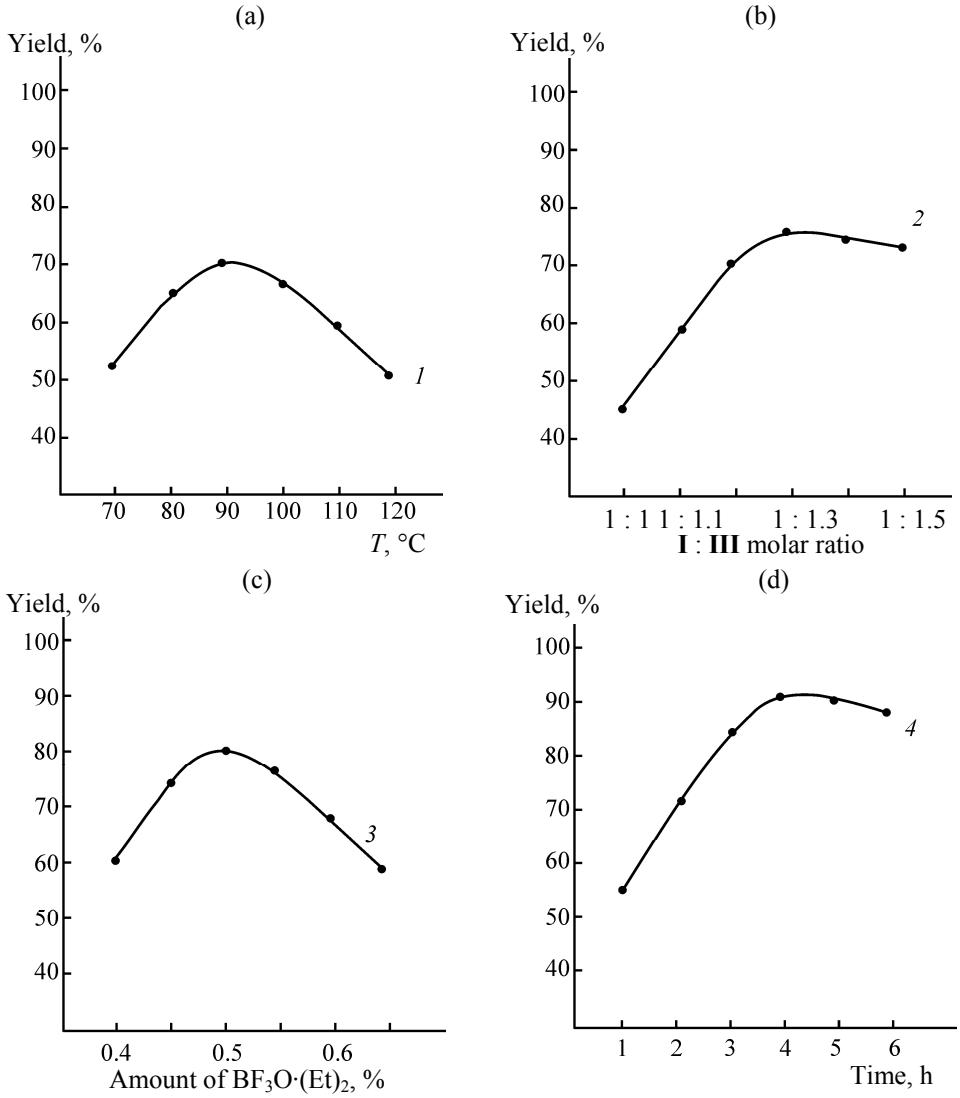
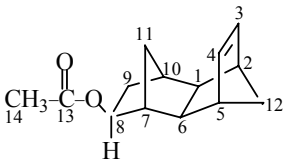
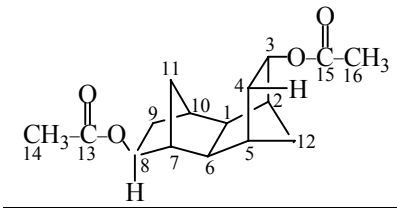


Fig. 1. (a) Dependence of the diacetate **IX** yield on temperature, (b) molar ratio of reagents **I** : **III**, (c) amount of the boron trifluoride etherate catalyst, (d) and the reaction time.

Table 1. Yields, physicochemical constants, and elemental analysis data of the synthesized diesters of tetracyclododecan-3,8-diol and saturated acids

Acid C_1–C_5	Diester	Yield, %	Physicochemical constants			Found, %		Formula	Calculated, %	
			bp, °C (1 mmHg)	d_4^{20}	n_D^{20}	C	H		C	H
II	**VIII**	93.0	148–151	1.1821	1.5006	68.02	7.52	$C_{15}H_{20}O_4$	68.16	7.63
III	**IX**	90.0	162–165	1.1204	1.5038	68.91	7.87	$C_{16}H_{22}O_4$	69.05	7.97
IV	**X**	84.9	171–174	1.1108	1.5049	69.71	8.19	$C_{17}H_{24}O_4$	69.84	8.27
V	**XI**	76.5	186–188	1.1088	1.5068	70.44	8.50	$C_{18}H_{26}O_4$	70.56	8.55
VI	**XII**	70.4	170–173	1.1015	1.5038	70.39	8.45	$C_{18}H_{26}O_4$	70.56	8.55
VII	**XIII**	68.1	193–195	1.1001	1.5011	71.18	8.70	$C_{19}H_{28}O_4$	71.32	8.81

Table 2. Parameters of the IR and ^{13}C NMR spectra of compounds **I** and **IX**

Structure	ν, cm^{-1}	δ_C, ppm
	2800–3000 (CH, CH_2), 3100, 1645 (HC=CH), 1730 (C=O), 1380 (CH_3) 1100–1250 (C–O–C)	165.81 (C^{13}), 136.40 (C^3), 135.85 (C^4), 59.61 (C^8), 53.44 (C^2), 50.20 (C^5), 48.50 (C^6), 47.12 (C^1), 47.05 (C^7), 43.60 (C^{10}), 40.56 (C^9), 36.71 (C^{11}), 34.46 (C^{12}), 17.88 (C^{14})
	705, 1440, 1366, 2938 (CH_2, CH_3); 1017, 1056, 1233, 1292 (C–O–C), 1730 (C=O)	163.75 (C^{13}), 164.52 (C^{15}), 78.12 (C^3), 77.45 (C^8), 35.91 (C^4), 32.45 (C^9), 52.45 (C^2), 49.82 (C^5), 40.05 (C^1), 38.91 (C^6), 35.6 (C^7), 34.55 (C^{10}), 28.01 (C^{11}), 27.85 (C^{12}), 18.92 (C^{14}), 19.62 (C^{15})

From the presented data it is seen that the yield diesters of tetracyclododecan-3,8-diol decreases from 93.0 to 68.1% at the increase in molecular mass of the acid from formic to *n*-valeric one. Hence, the activity of the acids in the addition to the double bond of cycloalkene **I** decreases with the increase in the length of the saturated residue.

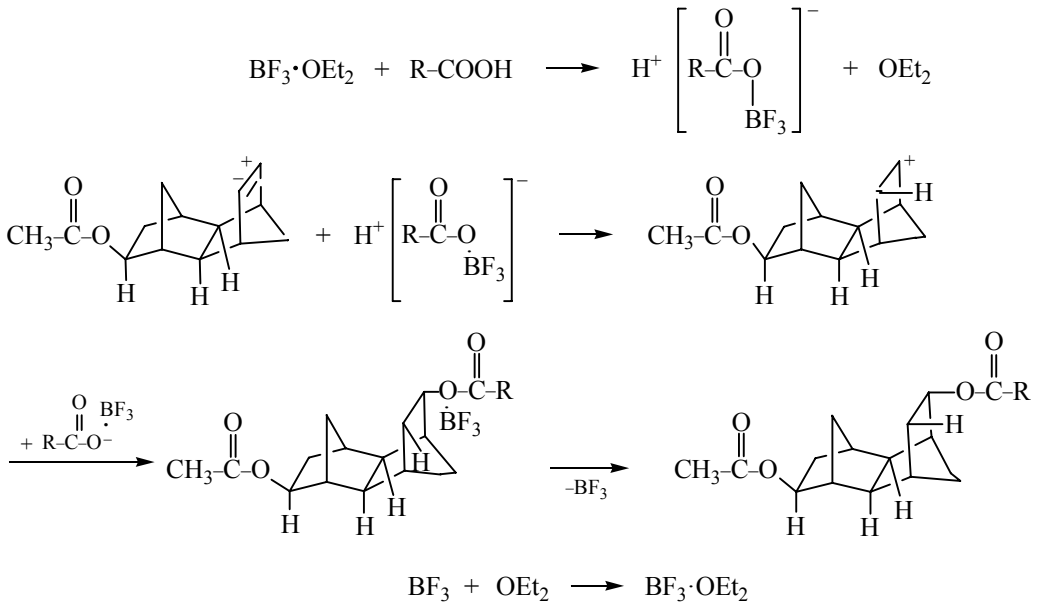
The structure of the synthesized esters **I** and **IX** was established by the IR and the ^{13}C NMR spectra (see Table 2).

In the ^{1}H NMR spectra of esters signals of *endo-endo*- isomers are observed at 4.2–4.6 ppm, and of *exo-exo* ones, at 6.1–6.3 ppm. After the isomerization the signals of *endo-endo* isomer are absent.

Considering these data the following mechanism of formation diesters on the basis of unsaturated tetracyclic monoesters and monobasic saturated acids in the presence of boron trifluoride etherate catalyst (Scheme 3) have been suggested.

The diesters obtained are colorless viscous oils. They may be used as additives to synthetic oils and the aromatic substances in the perfumeric industry.

Scheme 3.



EXPERIMENTAL

IR spectra were obtained on a Bruker Alpha spectrometer (Germany) in the range 600–4000 cm^{-1}. NMR spectra were taken on a Bruker AV-300 spectrometer (300 MHz) in acetone-d_6.

The composition and purity of starting substances and the diesters synthesized was evaluated by GLC on an LKhM-8MD chromatograph, stationary phase 10% of polyethyleneglycol disuccinate on spherochrom, column 1.5 m, carrier gas helium, flow rate 50 mL/min, temperatures of evaporator, column, and detector 250, 190, and 150°C respectively, detector current 120 mA.

Tricyclo[5.2.1.$0^{2.6}$]deca-3,8-diene, vinyl acetate, and starting saturated acids were freshly distilled. Their physicochemical properties were in agreement with the reported data [8–10].

Synthesis of acetate (I). The equimolar mixture of tricyclo[5.2.1.$0^{2.6}$]deca-3,8-diene and vinyl acetate, 1.25 wt % of nano-TiO_2, and 0.2 wt % of hydroquinone with respect to tricyclo[5.2.1.$0^{2.6}$]deca-3,8-diene was heated at 190°C for 4 h in the hermetically closed steel swinging 1 L pressure reactor. After the reaction was complete the reactor was cooled to room temperature, the catalyst was filtered off, and the filtrate was distilled first at atmospheric pressure and then in a vacuum. Physicochemical constants of acetate **I** were as follows: bp 122–124°C (2 mmHg), d_4^{20} 1.1152, n_D^{20} 1.5012.

Addition of aliphatic acids to *exo-exo*-8-asetoxytetracyclo[4.4.1$^{2.5}$.1$^{7.10}$.0$^{1.6}$]dodec-3-ene (I) *(general procedure)*. The mixture of 1 mol of compound **I**, 0.3 mol of the acid, and 1.0 g of boron trifluoride etherate was heated for 4 h at 90°C. After the completion of the reaction the obtained mixture was washed with distilled water and dried over sodium sulfate. Then it was distilled in a vacuum. Yields of the products, their physicochemical characteristics and elemental analysis data are presented in Table 1.

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