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ADDITION OF ALCOHOLS AND ACIDS TO OLEFINS IN PRESENCE OF ZEOLITE CATALYST H-BETA

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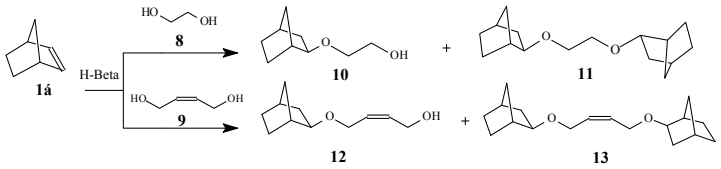
By studying the reactions of styrene and norbornene with different alcohols and carbonic acids in the presence of heterogenic catalyst, it was found that the selected zeolite H-Beta is an active and selective catalyst for these reactions. Ethers and esters of norbornene have exo-configuration. It has been established that reaction of norbornene with diols, catalyzing by zeolite Beta, leads to the formation of esters, which have not been found before.



INTRODUCTION

Addition of alcohols and ethers to the multiple carbon-carbon bonds in the presence of homogeneous and heterogeneous catalysts finds a wide application in synthesis of ethers and esters.[1] The use of homogeneous (mineral acids) and heterogeneous (cationite) catalysts has some drawbacks and does not provide the required high yields and selectivity of products. We investigated these reactions in the presence of industrial available zeolite catalyst H-Beta, which is successfully used in petrochemical processes alkylation, isomerization and so on.[2, 3]

RESULTS AND DISCUSSION

In the present work we found (Scheme 1) that monohydric alcohols (**2-4**) of various structures (butyl, allylic, benzyl) are connected to styrene (**1a**) and norbornene (**1б**) selectivity with the formation of corresponding ethers (**5а,б, 6а,б, 7а,б**).

In the studied conditions (Table 1) there is a total conversion of olefin. Selectivity of formation of target ethers is more than 85%, which is weakly dependent on the structure of reagents.

In the case reaction of diols (**8,9**) with norbornene the reaction proceeds by consistent formation of mono- (**10, 12**) and diethers (**11, 13**) in the presence of zeolite H-Beta (Scheme 2).

Increasing the temperature from 50^0C to 80^0C the conversion of norbornene **1b** is changed slightly. However, selectivity of diethers' formation increases from 4% to 32%. Moreover increasing the molar ratio olefin : diol from 1:3 to 3:1 selectivity of diethers' formation increases by more than twice (Table 2).

In the studied conditions the activities of ethylene glycol (**8**) and *cis*-2-butene-1,4-diol (**9**) are similar. Bicyclic olefin **1b** reacts quantitatively with monohydric acids (**14-17**) producing appropriate esters. These yields are 80-99% (a four-fold molar excess of acid) and depend on the identity of acids.

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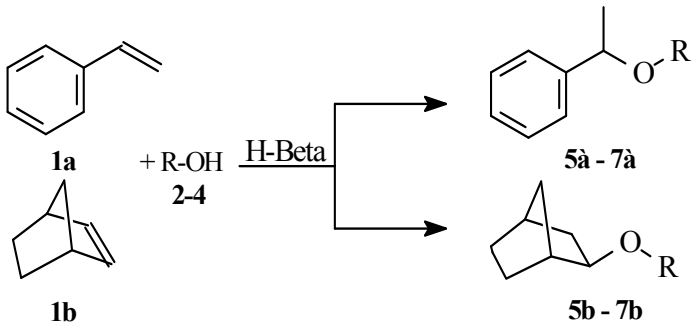
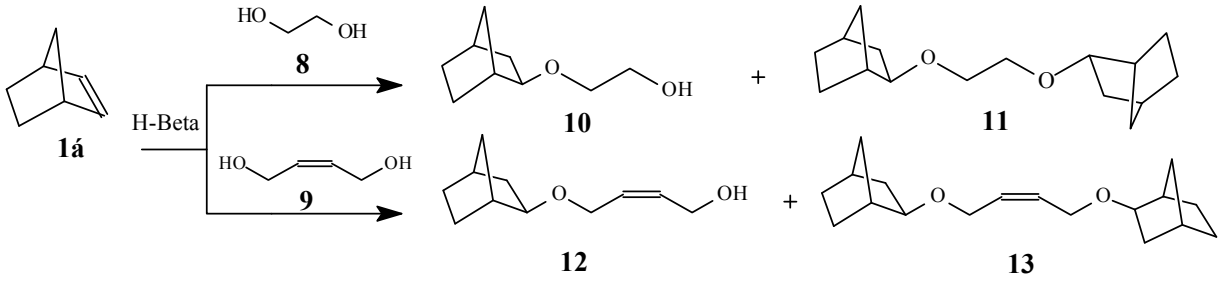


R= n-Bu (**2; 5à, b**); All (**3; 6à, b**); Bn (**4; 7à, b**)

Scheme 1 – Formation of ethers **(5a,б-7a,б)** by reaction of alcohols and olefins **1a,б**.

Table 1
Reaction of olefins **1a,b** with alcohols **2-4** in presence zeolite H-Beta
(molar ratio olefin : alcohol = 1 : 3, 20 wt% catalyst, T=80^{0}C, 5 h)

Olefin	Alcohol	Selectivity, %
1a	**2**	**5a** (92)
1b	**2**	**5b** (93)
1a	**3**	**6a** (89)
1b	**3**	**6b** (90)
1a	**4**	**7a** (92)
1b	**4**	**7b** (95)



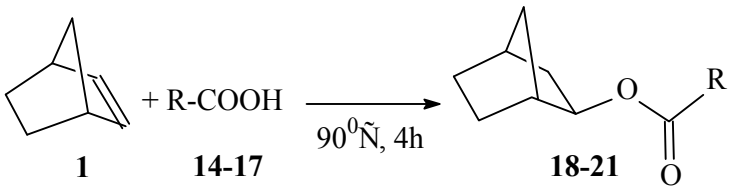
Scheme 2 – Formation of mono- and diethers of norbornene over zeolite H-Beta.

Table 2
Reaction of norbornene with diols **8, 9** (molar ratio **1б** : diol = **A:B**, 20% wt. catalyst H-Beta, 5 h)

Diol	**A:B**	T,ºC	Selectivity, %	
			Monoether	Diether
HÎ Î Í **8**	1:3	50	Î Î í **10** (92)	**11** (4)
		60	Î Î í **10** (84)	**11** (12)
		80	Î Î í **10** (58)	**11** (32)

Table 2 (continued)

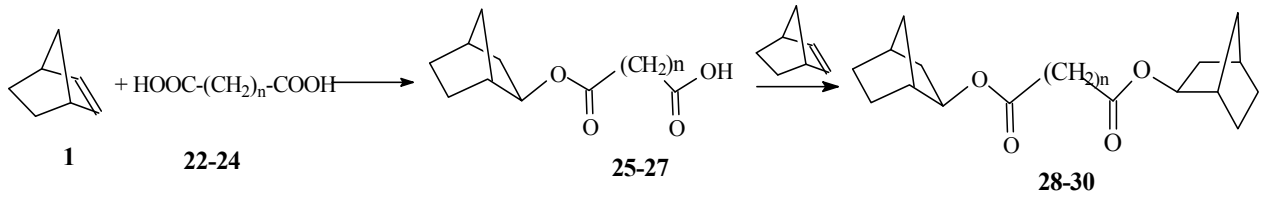
HO⁄⁄OH **9**	3:1	80	**12** (25)	**13** (68)
	1:1		**12** (46)	**13** (41)
	1:3		**12** (60)	**13** (30)



1 **14-17** **18-21**

R= -CH_3 (**14, 18**); -n-C_3H_7 (**15, 19**); -CH_2Cl (**16, 20**); -C_3H_5(**17, 21**)

Scheme 3 – Formation of esters **(18-21)** by reacting monobasic carboxylic acids **(14-17)** with norbornene **1b**.



1 **22-24** **25-27** **28-30**

n = 0 (**22, 25, 28**); 1 (**23, 26, 29**); 2 (**24, 27, 30**)

Scheme 4 – Formation esters **(25-27)** by react monocarbonic acids **(22-24)** with norbornene **1b**.

At the same time, judging from yield of monoethers, monochloracetic **16** and methacrylic **17** acids are six times less active than acetic acid **14**.

The reaction of olefin **1b** and dicarbonic acids is going to with the formation mono- and diethers appropriately (Scheme 4).

Spatial structure of diesters of norbornene (**28-30**) identified by methods of homo- (COSY, NOESY) and heteronuclear (HSQC, HMBC) two-dimensional ^1H, ^{13}C NMR spectroscopy. So, in ^{13}C NMR spectra of target esters (**28-30**), signals of atoms C-7 of bicyclic fragment are situated in the range of 35.6…36.2 ppm area, indicating that *exo*-configuration is because of signals *endo*-isomers located in the weaker field (~40 ppm area).

EXPERIMENTAL

Chromatographic analysis of the products was performed on a Carlo Elba HRGS 5300 Mega Series chromatograph with a flame ionization detector using helium as the carrier gas at a flow rate of 30 mL/min, a SE 30 coated column of a 25 m length, and the column temperature programmed from 50 to 280°C at a rate of 8°C/min. Mass chromatograms were recorded on Fisons (50 m fused silica capillary column DB 560) and Focus instruments with a Finingan DSQ II mass spectrometric detector (ion source temperature, 200°C; on column injection temperature, 50–270°C; heating rate, 10°C/min; Thermo TR 5MS column, 50 × 2.5 × 10^{-4} m; helium flow rate, 0.7 mL/min). The mass spectra of the compounds were obtained in the electron ionization mode. NMR spectra were recorded on a Bruker AVANCE-400 (^1H 400.13 MHz) spectrometer in $CDCl_3$, using benzene d_6 and toluene d_8 as an internal standard. One and two dimensional NMR spectra were recorded using standard pulse sequences. 2D homonuclear (COSY HH, NOESY) and heteronuclear (HSQC, HMBS) correlation experiments were carried out using pulsed field gradient techniques.

In order to carry out the reactions, zeolite BEA (Beta) (mole ratio SiO_2/Al_2O_3 = 18.0), synthesized in the JSC "Angarsk Catalysts and Organic Synthesis" in NH_4-form, was used as catalyst. Zeolite Beta was formed to H-form by heated in air at 540ºC for 3 h. Before experiments the catalyst sample was dried in air for 4 h at 350ºC.

1. Method of reaction of olefins (**1a,b**) with alcohols (**2-4**)

A mixture of 0.255 M alcohol **2** (or 0.255 M alcohol **3,** or 0.255 M alcohols **4**) and 0.085 M norbornene **1b,** 20% wt. catalyst H-Beta was carried out at 80°C and mixed intensively for 5 h. The reaction mass was separated from the catalyst by filtering after the reaction termination and unreacted alcohol was removed at a low pressure. Ethers were isolated by vacuum distillation for calibration.

1-n-butyl-1-phenylethan (**5a**). b.p. 95-96°C (10 mm Hg). ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 0.86 (t, 3H, CH_3), 1.33 (m, 2H, CH_2), 1.35 (m, 2H, CH_2), 1.45 (d, 3H, CH_3), 3.42 (q, 2H, OCH_2), 4.30 (q, 1H, CH), 7.3 (m, 5H, ArH). ^{13}C-NMR ($CDCl_3$, δ ppm): 13.78 C^6, 18.90 C^5, 21.15 C^2, 32.65 C^4, 69.75 C^3, 72.86 C^1, 124.97-127.04 Ar, 143.03 $C^{1'}$.

1-allyloxy-1-phenylethan (**6a**): b.p. 68°C (5 mm Hg): ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 1.5 (d, 3H, CH_3), 3.85 (dddd., 1H, CH_a, ^2J 12.8, ^3J 5.8), 3.94 (dddd., 1H, CH_b, ^2J 12.8, ^3J 5.2), 4.51 (dd., 1H, CH, ^3J 6.4), 5.19 (dd., 1H, CH_a, ^2J 1.6, ^3J 10.4), 5.29 (dd., 1H, CH_b, ^2J 1.6, ^3J 17.2), 5.95 (dddd., 1H, CH, ^3J 5.2, ^3J 5.8, ^3J 10.4, ^3J 17.2), 7.28-7.40 (m., 5H, Ar).

1-cyclohexyloxy-1-phenylethan (**7a**). b.p. 91-92°C (9 mm Hg): ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 1.46 (d, 3H, CH_3), 1.12-1.20 (m, 6H, CH_2), 1.78-1.94 (m, 4H, CH_2), 3.40 (m, 1H, CH), 4.64 (q, 1H, ArCH), 7.23-7.33 (m, 5H, ArH).

Exo-2-(butoxy)bicyclo[2.2.1]heptane **(5б)**. b.p. 77 °C (27 mm Hg). ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 0.91 (m, 3H, CH_3), 0.96-1.07 (m, 3H, CH_2), 1.32-1.41 (m, 3H, CH_2), 1.46-1.55 (m, 4H, CH_2), 2.20 (s, 1H, CH), 2.29 (d, 1H, CH, ^2J=4), 3.24-3.40 (m, 1H, CH), 3.24-3.40 (m, 2H, CH_2). MS (70eV), m/z (*J., %*): 168 $[M-1]^+$ (≤1), 94 (100); 66 (74); 79 (65); 67 (56), 41 (49), 95 (39), 57 (28), 83 (19), 55 (17), 68 (16), 56 (13), 112 (12).

2-(alliloxy)bicyclo[2.2.1]heptane **(6б)**. b.p. 78°C (10 mm Hg). ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 0.95-1.12 (m, 3H, CH_2), 1.37-1.60 (m, 5H, CH_2), 2.25 (s, 1H, CH), 2.33 (d, 1H, CH), 3.89-4.00 (m, 2H, CH_2), 5.10-5.18 (d, 1H, CH_a, ^2J=1.6, ^3J=10.4), 5.22-5.32 (d, 1H, CH_b, ^2J=1.6, ^3J=17.2), 5.83-5.99 (m, 1H, CH). MS (70eV), m/z (*J., %*): 152 $[M-1]^+$ (1), 67 (100); 41 (56); 94 (51); 95 (41), 66 (34), 79 (29), 55 (27), 93 (23), 91 (11), 81 (11), 77 (11).

2-(benzyloxy)bicyclo[2.2.1]heptane **(7б)**. b.p. 70 °C (20 mm Hg). ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 0.92-1.05 (m, 3H, CH_2), 1.25-1.40 (m, 2H, CH_2), 1.51-1.56 (m, 3H, CH_2), 2.19 (s, 1H, CH), 2.28 (s, 1H, CH), 3.64-4.51 (m, 1H, CH), 3.64-4.51 (m, 2H, CH_2), 7.00-7.05 (m, 5H, Ar).

2-(bicyclo[2.2.1]heptyl-2-oxy)ethanol **(10)**. b.p. 130°C (10 mm Hg). ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 0.95-1.10 (m, 3H, CH_2), 1.38-1.59 (m, 5H, CH_2), 2.23 (m, 1H, CH), 2.33 (m, 1H, CH), 2.55 (1H, OH), 3.39 (d, 1H, CH), 3.49-3.57 (m, 2H, CH_2), 3.70-3.77 (m, 2H, CH_2). ^{13}C-NMR ($CDCl_3$, δ ppm): 24.61 C^6, 28.55 C^5, 34.77 C^7, 35.17 C^4, 39.56 C^3, 40.36 C^1, 63.71 C^9, 67.66 C^8, 83.0 C^2. MS (70eV), m/z (*J., %*): 156 $[M-1]^+$ (2), 95 (100); 67 (49); 155 (19), 111 (18), 94 (16), 94 (15), 66 (15), 41 (15).

2,2'-[ethane-1,2-diylbis(oxy)]bicyclo[2.2.1]heptane **(11)**. b.p. 158°C (5 mm Hg). ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 0.86-1.26 (m, 8H, CH_2), 1.32-1.40 (m, 8H, CH_2), 1.55-1.58 (m, 2H, CH_2), 1.63 (m, 1H, CH), 1.73 (m, 2H, CH_2), 2.04 (m, 2H, CH, CH), 3.20 (m, 2H, CH_2), 3.42 (m, 2H, CH_2), 3.57 (d, 1H, CH). MS (70eV), m/z (*J., %*): 250 $[M-1]^+$ (1), 95 (100); 94 (95); 66 (87), 79 (77), 67 (52), 45 (47), 41 (33), 55 (19), 57 (18); 83 (17); 44 (16); 77 (13); 65 (13); 43 (14); 53 (11).

Exo-4-(bicyclo[2.2.1]hept-2-yloxy)but-2-en-1-ol **(12)**. b.p. 141 °C (2 mm Hg). ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 0.95-1.03 (m, 2H, C^6H_b, C^3H_a), 1.03-1.14 (m, 2H, C^6H_a, C^3H_b), 1.37-1.48 (m, 1H, C^5H_b), 1.50-1.60 (m, 1H, C^5H_a), 2.17 (s, 1H, C^1H), 2.25 (s, 1H, -OH), 2.34 (d, 1H, C^4H), 3.40 (d, 1H, C^2H), 3.95-4.09 (m, 1H, C^8H_a), 4.19(m, 1H, C^8H_b, ^2J=6.4, ^3J=18.8), 4.22 (d, 2H, $C^{11}H_a$, $C^{11}H_b$, ^2J=4.4 ^3J=16.8), 5.67-5.75 (m, 1H, C^9H), 5.76-5.85 (m, 1H, $C^{10}H$). ^{13}C-NMR ($CDCl_3$, δ ppm): 24.58 C^6, 28.40 C^5, 35.14 C^4, 39.51 C^3, 40.28 C^1, 58.53 C^{11}, 64.03 C^8, 82.67 C^2, 128.82 C^{10}, 131.82 C^9. MS (70eV), m/z (*J., %*): 182 $[M-1]^+$ (2), 164 (7), 138 (12), 109 (12), 95 (100), 94 (22), 81(18), 79 (46), 77 (10), 71 (17), 70 (27), 67 (90), 66 (40), 57 (10), 55 (27), 53 (18), 43 (40).

Exo-exo-[(2Z)-but-2-en-1,4-diylbis(oxy)]bisbicyclo[2.2.1] heptane **(13)**. b.p. 183°C (2 mm Hg). ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 0.97-1.12 (m, 6H, C^6H_a, $C^{14}H_a$, C^5H_a, $C^{17}H_a$, C^7H_a, $C^{18}H_a$), 1.34-1.48 (m, 6H, C^3H_a, $C^{14}H_a$, C^5H_b, $C^{16}H_b$, C^6H_b, $C^{17}H_b$), 1.49-1.58 (m, 4H, C^7H_b, $C^{18}H_b$, C^3H_b, $C^{14}H_b$), 2.23 (s, 2H, C^4H, $C^{15}H$), 2.30-2.34 (d, 2H, C^1H, $C^{12}H$), 3.35-3.40 (dd, 2H, C^2H, $C^{13}H$), 3.95-4.05 (m, 2H, C^8H_a, C^8H_b), 4.09 (dd, 1H, $C^{11}H_a$), 4.19 (dd, 1H, $C^{11}H_b$), 5.63-5.74 (m, 1H, $C^{10}H$), 5.75-5.88 (m, 1H, C^9H). ^{13}C-NMR ($CDCl_3$, δ ppm): 23.75 C^6, 27.62 C^5, 33.93 C^7, 34.27 C^4, 38.71 C^3, 39.42 C^1, 57.54 C^{11}, 63.04 C^8, 81.25 C^2, 129.41C^{10}, 131.96 C^9. MS (70eV), m/z (*J., %*): 276 $[M-1]^+$ (<1), 164 (6), 96 (10), 95 (100), 93 (6), 79 (6), 70 (10), 67 (42), 41 (13).

2. Method of reaction of norbornene (**1b**) with monocarboxylic acids (**14-17**)

A mixture of 0,34 M acetic acid **14** (or 0.34 M *n*-butyric acid **15**, or 0.34 M chloracetic acid **16**, or 0.34 M methacrylic acid **17**), 0.085 M of norbornene, 20% wt. catalyst H-Beta was carried out at 90°C and mixed intensively for 4 h. For homogenization of initial compounds (**16, 17**) nonane was used as a solvent. The reaction mass was separated from the catalyst by filtering after the reaction termination and unreacted acid was removed at a low pressure. Esters were isolated by vacuum distillation for calibration.

Exo-bicyclo[2.2.1]hept-2-yl ester of acetic acid **(18)**. b.p. 95°C (20 mm Hg). ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 1.08-1.18 (m, 4H, C^3H_a, C^6H_a, C^6H_b, C^3H_b), 1.42-1.54 (m, 3H, C^4H_b, C^7H_a, C^7H_b), 1.73 (m, 1H, C^4H_a), 2.02 (s, 3H, C^9H_3), 2.30 (m, 2H, C^2H, C^5H), 4.61 (d, 1H, C^1H). ^{13}C-NMR ($CDCl_3$, δ ppm): 21.42 C^9, 24.33 C^3, 28.13 C^4, 35.24 C^5, 35.37 C^7, 39.60 C^6, 41.40 C^2, 77.60 C^1, 170.82 C^8. MS (70eV), m/z (*J., %*): $[M-1]^+$ 154 (6), 43 (100), 66/67 (70/68), 94/95 (68/52), 79 (65), 111/112 (64/51), 41 (53), 71 (52).

Exo-bicyclo[2.2.1]hept-2-yl ester of n-butyric acid **(19)**. b.p. 106°C (10 mm Hg). ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 0.96 3 (t, 3H, $C^{11}H_3$), 1.17-1.20 (m, 3H, C^3H_a, C^7H_a, C^4H_a), 1.39-1.49 (m, 2 H, C^6H_a, C^4H_b), 1.50-1.58 (m, 2H, C^7H_b, C^3H_b), 1.65 (m, 2H, $C^{10}H_2$), 1.69-1.78 (m, 1H, C^6H_b), 2.25 (t, 2H, C^9H_a, C^9H_b), 2.27-2.32 (m, 2H, C^5H, C^2H), 4.62 (d, 1H, C^1H). ^{13}C-NMR ($CDCl_3$, δ ppm): 13.66 C^{11}, 18.54 C^{10}, 24.31 C^3, 28.85 C^4, 35.26 C^7, 35.38 C^9, 36.59 C^5, 39.65 C^6, 41.45 C^2, 77.29 C^1, 173.40 C^8. MS (70eV), m/z (*J., %*): $[M-1]^+$ 182 (2), 71 (100), 95 (52), 43 (40), 139 (31), 111 (30), 154 (15), 79 (12).

Exo-bicyclo[2.2.1]hept-2-yl ester of chloracetic acid **(20)**. b.p. 95°C (6 mm Hg). ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 1.09-1.22 (m, 3H, C^3H_b, C^7H_b, C^4H_b), 1.44-1.57 (m, 4H, C^3H_a, C^4H_a, C^7H_a, C^6H_a), 1.75-1.80 (m, 1H, C^6H_b), 2.32 (m, 1H, C^5H), 2.36 (d, 1H, C^2H), 4.04 (s, 2H, C^9H_a, C^9H_b), 4.72 (d, 2H, C^1H). ^{13}C-NMR ($CDCl_3$, δ ppm): 24.13 C^6, 28.03 C^5, 35.23 C^7, 35.35 C^4, 39.38 C^3, 41.20 C^9, 41.39 C^1, 79.71 C^2, 167.01 C^8. MS (70eV), m/z (*J., %*): $[M-1]^+$ 188 (<1), 66/67/68 (100/78/29), 94/95 (56/64), 77/79 (38/87), 41 (40), 49 (20), 55 (17), 42 (13), 53 (10).

Exo-bicyclo[2.2.1]hept-2-yl ester of methacrylic acid **(21)**. b.p. 90°C (6 mm Hg). ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 1.12-1.20 (m, 3H, C^3H_a, C^4H_a, C^7H_a), 1.43-1.57 (m, 4H, C^3H_b, C^4H_b, C^6H_a, C^7H_a), 1.74-1.79 (m, 1H, C^6H_b), 1.93 (s, 3H, $C^{11}H_3$), 2.31 (m, 1H, C^5H), 2.35 (m, 1H, C^2H), 4.68 (m, 1H, C^1H), 5.52 (s, 1H, $C^{10}H_a$), 6.07 (s, 1H, $C^{10}H_b$). ^{13}C-NMR ($CDCl_3$, δ ppm): 18.26 C^{11}, 24.24 C^3, 28.17 C^4, 35.33 C^7, 35.37 C^5, 39.57 C^6, 41.45 C^2, 77.74 C^1, 124.81 C^{10}, 136.90 C^9, 167.09 C^8. MS (70eV), m/z (*J., %*): $[M-1]^+$ 180 (<1), 69 (100), 41 (84), 66 (71), 94 (56), 95 (40), 79 (19), 70 (19), 109 (11), 97 (11), 55 (10), 124 (10), 137 (10).

3. Method of reaction of norbornene (**1b**) with dicarboxylic acids (**22-24**)

A mixture of 0.34 M oxalic acid **22** (or 0.34 M malonic acid **23**, or 0.34 M succinic acid **24**), 0.085 M of norbornene**,** 20% wt. catalyst H-Beta was carried out at 90°C and mixed intensively for 4 h. For homogenization of initial compounds (**22-24**) nonane was used as a solvent. The reaction mass was separated from the catalyst by filtering after the reaction termination and unreacted acid was removed at a low pressure. Esters were isolated by vacuum distillation for calibration.

The resulting physic-chemical properties, NMR-spectra and mass-spectra of compounds **25-27** correspond to literature data.[4]

Exo-dibicyclo[2.2.1]hept-2-yl ester of oxalic acid **(28)**. b.p. 122°C (7 mm Hg). ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 1.12-1.23 (m, 6H, C^6H_a, C^5H_a, C^7H_a, $C^{15}H_a$, $C^{14}H_a$, $C^{16}H_a$), 1.44-1.62 (m, 8H, C^6H_b, C^5H_b, C^3H_a, C^7H_b, $C^{15}H_b$, $C^{14}H_b$, $C^{12}H_a$, $C^{16}H_b$), 1.76-1.82 (dddd, 2H, C^3H_b, $C^{12}H_b$), 2.33 (s, 2H, C^4H, $C^{13}H$), 2.43 (d, 2H, C^1H, $C^{10}H$), 4.75 (d, 2H, C^2H, $C^{11}H$). ^{13}C-NMR ($CDCl_3$, δ ppm): 24.11 C^3, C^{15}, 28.03 C^5, C^{14}, 35.29 C^7, C^{16}, 35.37 C^4, C^{13}, 39.26 C^3,C^{12}, 41.30 C^1, C^{10}, 80.46 C^2, C^{11}, 158.05 C^8, C^9. MS (70eV), m/z (*J., %*): $[M-1]^+$ 278 (0.1), 95/96 (100/8), 66/67/68 (8/24/2), 41 (9), 77/79 (3/4), 93 (4), 53/55 (2/4), 65 (3).

Exo-dibicyclo[2.2.1]hept-2-yl ester of malonic acid **(29)**. b.p. 172°C (2 mm Hg). ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 1.08-1.19 (m, 6H, C^5H_a, $C^{15}H_a$, C^6H_a, $C^{16}H_a$, C^7H_a, $C^{17}H_a$), 1.43-1.59 (m, 8H, C^3H_a, $C^{13}H_a$, C^7H_b, $C^{17}H_b$, C^5H_b, $C^{15}H_b$, C^6H_b, $C^{16}H_b$), 1.72-1.77 (m, 2H, C^3H_b, $C^{13}H_b$), 2.30 (s, 2H, C^4H, $C^{14}H$), 2.35 (s, 2H, C^1H, $C^{11}H$), 3.29 (s, 2H, C^9H_a, C^9H_b), 4.67 (d, 2H, C^2H, $C^{12}H$). ^{13}C-NMR ($CDCl_3$, δ ppm): 24.18 C^6, C^{16}, 28.10 C^5, C^{15}, 35.24 C^7, C^{17}, 35.34 C^4, C^{14}, 39.34 C^3,C^{13}, 41.33 C^1, C^{11}, 42.26 C^9, 78.79 C^2, C^{12}, 166.34 C^8, C^{10}. MS (70eV), m/z (*J., %*): $[M-1]^+$ 292 (0.2), 95 (100), 67 (13), 111 (10), 199 (8).

Exo-dibicyclo[2.2.1]hept-2-yl ester of succinic acid **(30)**. b.p. 180°C (1 mm Hg). ^{1}H-NMR ($CDCl_3$, δ ppm, *J*Hz): 1.12-1.24 (m, 6H, C^7H_a, C^5H_a, $C^{16}H_a$, C^6H_a, $C^{17}H_a$, $C^{18}H_a$), 1.42-1.53 (m, 8H, $C^{14}H_a$, C^3H_a, C^5H_b, $C^{16}H_b$, C^7H_a, $C^{18}H_b$, C^6H_b, $C^{17}H_b$), 1.70-1.75 (m, 2H, C^3H_b, $C^{14}H_b$), 2.29 (m, 4H, C^4H, $C^{15}H$, C^1H, $C^{12}H$), 2.57 (m, 4H, C^9H_a, C^9H_b, $C^{10}H_a$, $C^{10}H_b$), 4.63 (d, 2H, C^2H, $C^{13}H$). ^{13}C-NMR ($CDCl_3$, δ ppm): 24.25 C^6, C^{17}, 28.13 C^5, C^{16}, 29.58 C^9, C^{10}, 35.25 C^7, C^{18}, 35.36 C^4,C^{15}, 39.52 C^3, C^{14}, 41.39 C^1, C^{12}, 77.89 C^2, C^{13}, 171.93 C^8, C^{11}. MS (70eV), m/z (*J., %*): $[M-1]^+$ 306 (0.1), 95 (100), 67 (24), 195 (18), 55 (9), 79 (9), 111 (9), 213(9), 41 (7), 162 (7).

CONCLUSIONS

The obtained results indicate that the zeolite H-Beta is an active and selective catalyst for synthesis of ethers and esters from olefins with acids and alcohols.

It should be noted that the offered methods are simply compared to methods based on the use of traditional acid catalysts. In this case products of reactions are separated from the catalyst by filtering and zeolite H-Beta can be recovered for use later.

Besides high activity and selectivity, zeolite catalyst H-Beta makes it possible to obtain new structure compounds, which were not obtained using homogeneous acidic catalysts[5].

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