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Synthesis and Transformations of Norbornyl Acrylates

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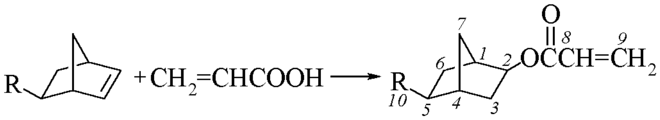
Abstract—A simple and more environmentally friendly procedure than that traditionally used was developed for preparation of esters consisting in acrylic acid addition to bicyclo[2.2.1]hept-2-ene and its 5-alkyl derivatives. The acrylates obtained were subjected to hydrogenetion followed by hydrolysis of propionic acid esters. A number of new compounds was obtained; some among them possess a pleasant odor.

Esters of cyclic alcohols and acrylic acid are successfully used as monomers for plastics [1, 2], efficient adhesive for dental prostheses [3], compounds for protection from the action of UV light and paint binder at electronic printing [4], and also in preparation of nonaqueous polymer materials [5].

We developed a simple and more environmentally friendly procedure than that traditionally used for preparation of acrylic acid esters by thermal addition of the acid to bicyclo[2.2.1]hept-2-ene and its 5-*exo*-alkyl derivatives. The initial bicycloolefins were obtained by isomerization of a mixture of the *endo* and *exo* isomers in the presence of $AlCl_3$ in dichloromethane solution.



I–VI

R = H (**I**), Me (**II**), Et (**III**), *i*-Pr (**IV**), Pr (**V**), Bu (**VI**).

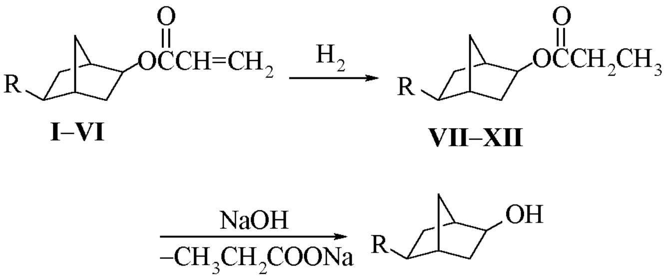
Acrylic acid same as saturated monocarboxylic acids [7–9] stereoselectively adds at heating without catalyst to bicyclo[2.2.1]hept-2-ene to yield an *exo* isomer of ester **I**. Compound **I** smells of pleasant odor with fruit tint and may be used as a component of synthetic perfumes.

The investigation of the composition and purity of the esters obtained by GLC revealed that the thermal addition of acrylic acid to the 5-*exo*-alkyl derivatives of norbornene resulted in formation of 5-*exo*-alkylbicyclo[2.2.1]hept-2-yl *exo*-acrylates (**II–VI**) as 92–94% of the product and 6-*exo*-alkylbicyclo[2.2.1]hept-2-yl *exo*-acrylates as 6–8% in the ratio 93 : 7. We used in reaction hyroquinone as inhibitor to prevent the radical polymerization of the acrylic acid at heating. The conditions of reaction and reagents ratio were optimized for ester formation; the best conditions were as follows: temperature 170°C, molar ratio of bicyclic olefins to acrylic acid 1 : 1.25, reaction time 3 h, hydroquinone in amount of 0.1 wt% to acrylic acid. Under these conditions the yields of acrylates reach 54–75%.

Alkyl substituents in the 5-position negatively affect the reactivity of the π-bond in the bicyclo[2.2.1]hept-2-ene ring. The longer is the hydrocarbon chain of the alkyl substituent, the lower is the yield of the corresponding acrylate:

$$H > CH_3 > CH_3CH_2 > CH_3CH_2CH_2 > (CH_3)_2CH$$
>CH3(CH2)3CH2.

Aiming at preparation of propionic acid esters with saturated bicyclic alcohols hydrogenation of acrylates **I–VI** was perfomed in the presence of Ni on kieselguhr as catalyst. The hydrogenated esters were also subjected to hydrolysis by 20% NaOH solution



I–VI **VII–XII** **XIII–XVIII**

R = H (**I, VII, XIII**), Me (**II, VIII, XIV**), Et (**III, IX, XV**), *i*-Pr (**IV, X, XVI**), Pr (**V, XI, XVII**), Bu (**VI, XII, XVIII**).

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Table 1. ^1H NMR spectra of compounds synthesized, δ, ppm

Compd. no.	H^1	H^2	H^3	H^4	H^5	H^6	H^7	H^8	H^9	H^{10}
I	2.20	4.60	1.40	2.20	1.0	1.10	1.13	6.23	5.75	–
II	2.20	4.60	1.45	2.25	5.0	1.15	1.15	6.18	5.76	0.85
VII	2.45	4.75	1.30	2.45	1.9	1.40	1.00	2.25	1.10	–
VIII	2.12	4.72	1.48	2.12	5.1	1.90	1.30	2.37	1.27	1.14
XIII	2.50	4.05	1.48	2.55	1.9	1.40	1.30	4.70	–	–
XIV	2.55	4.15	1.48	2.60	3.9	1.90	1.30	4.65	1.10	–

Table 2. Yields, physical properties and elemental analyses of norbornyl acrylates **I**–**VI**

Compd. no.	Yield, %	bp, °C (30 mm Hg)	d_4^{20}	n_D^{20}	Found, %		Formula	Calculated, %	
					C	H		C	H
I	75	108	1.0318	1.4740	72.24	8.46	$C_{10}H_{14}O_2$	72.26	8.89
II	68	117–118	0.9966	1.4755	73.29	8.91	$C_{11}H_{16}O_2$	73.30	8.94
III	65	136–137	0.9863	1.4785	74.17	9.30	$C_{12}H_{18}O_2$	74.19	9.33
IV	59	116–117	0.9710	1.4792	74.90	9.61	$C_{13}H_{20}O_2$	74.96	9.67
V	60	159–160	0.9827	1.4804	74.92	9.65	$C_{13}H_{20}O_2$	74.96	9.67
VI	54	179–180	0.9821	1.4860	75.60	9.95	$C_{14}H_{22}O_2$	75.63	9.97

along the known procedure [10]. We obtained as a result norbornyl propionates **VII–XII** in 94–95% yield and bicyclic alcohols **XIII–XVIII** in 96–98% yield.

The purity of compounds synthesized after distillation was 99–99.8%. Their isomeric composition and structure was investigated by means GLC, IR, and NMR spectroscopy. In the IR spectra of all acrylates appears a strong band in the 970 cm^{-1} region characteristic of an *exo* isomer. The absorption in the region 1725–1730 and 1240–1245 cm^{-1} evidences the presence of ester groups in the molecules, and the absorption bands at 815 and 890 cm^{-1} in combination with a band at 1640 cm^{-1} prove the presence of a vinyl group.

^1H NMR spectra of some compounds synthesized are presented in Table 1.

As seen from Table 1, in the spectra of acrylates **I, II** are observed signals at 5.75–6.23 ppm characteristic of vinyl protons; in the spectra of alcohols **XIII, XIV** appear the signals of hydroxy group protons at 4.65–4.70 ppm; the *endo*-protons H^2 and H^5 resonate in the 4.0–5.0 ppm region.

EXPERIMENTAL

The conditions used for GLC analysis and recording of ^1H,^{13}C, and IR spectra were described in our preceding communication [8].

As initial compounds were used the following bicyclo hydrocarbons: bicyclo[2.2.1]hept-2-ene, 5-methyl-, 5-ethyl-, 5-isopropyl-, and 5-butylbicyclo-[2.2.1]hept-2-enes. The compounds were obtained by condensation of olefins with cyclopentadiene [11]. The acrylic acid applied corresponded to specifications TU 6-09.413-83.

The synthesis of acrylates and their hydrogenation were carried out in a rotating pressure reactor of stainless steel; the hydrolysis of propionates was performed in the common glass vessels.

2-*exo*-Bicyclo[2.2.1]heptyl acrylate (I). A mixture of 47.1 g of norbornene, 45 g of acrylic acid, and 0.045 g of hydroquinone was heated in the pressure reactor to 170°C for 3 h. The fractional distillation of the resulting mixture afforded 61.9 g (75%) of compound **I**.

Compounds **II**–**VI** were prepared similarly (Table 2).

2-exo-Bicyclo[2.2.1]heptyl propionate (VII). A mixture of 33.2 g of compound **I**, 3.32 g of catalyst Ni on kieselguhr activated in a flow of hydrogen, and 0.33 g of hydroquinone was charged in the pressure reactor, and hydrogen was fed in to the pressure of 100 atm. The reactor was heated to 120°C for 2.5 h. After the hydrogen was no long consumed the

Table 3. Yields, physical properties and elemental analyses of norbornyl propionates **VII**–**XII**

Compd. no.	Yield, %	bp, °C (30 mm Hg)	d_4^{20}	n_D^{20}	Found, %		Formula	Calculated, %	
					C	H		C	H
VII	94	109.5	0.9996	1.4596	71.32	9.56	$C_{10}H_{16}O_2$	71.39	9.58
VIII	96	119–120	0.9894	1.4620	72.45	9.93	$C_{11}H_{18}O_2$	72.49	9.95
IX	98	137.0–137.5	0.9884	1.4630	73.40	10.25	$C_{12}H_{20}O_2$	73.43	10.27
X	96	145–146	0.9760	1.4600	74.20	10.51	$C_{13}H_{22}O_2$	74.24	10.54
XI	97	156.5–157.0	0.9868	1.4655	74.20	10.50	$C_{13}H_{22}O_2$	74.24	10.54
XII	98	177–178	0.9876	1.4666	75.60	10.74	$C_{14}H_{24}O_2$	75.63	10.78

Table 4. Yields, physical properties and elemental analyses of bicyclic alcohols **XIII**–**XVIII**

Compd. no.	Yield, %	bp, °C (30 mm Hg)	d_4^{20}	n_D^{20}	Found, %		Formula	Calculated, %	
					C	H		C	H
XIII	98	[a]	–	–	74.91	10.72	$C_7H_{12}O$	74.95	10.78
XIV	97	73–74	0.9988	1.4826	76.11	11.16	$C_8H_{14}O$	76.14	11.18
XV	94	98–99	0.9950	1.4836	77.00	11.50	$C_9H_{16}O$	77.08	11.50
XVI	94	122–123	0.9875	1.4890	77.81	11.72	$C_{10}H_{18}O$	77.86	11.76
XVII	95	117–118	0.9745	1.4790	77.72	11.72	$C_{10}H_{18}O$	77.86	11.76
XVIII	95	142–143	0.9738	1.4896	78.50	11.94	$C_{11}H_{20}O$	78.51	11.97

[a] Melting point of compound **XIII** 127°C is consistent with the published data [12].

catalyst was filtered off, and the reaction mixture was subjected to fractional distillation. Compound **VII** was obtained in 94% yield.

Compounds **VIII–XII** were prepared in the similar way (Table 3).

2-*exo*-Bicyclo[2.2.1]heptanol (XIII). To a mixture of 16.8 g of compound **VII** and 25 ml of ethanol at heating to 70°C while vigorous stirring was added within 1 h 20 ml of 20% NaOH solution. The stirring was continued for 1 h more. The reaction mixture was extracted with ether, the extract was dried with anhydrous $CaCl_2$, the solvent was distilled off. We obtained 11 g (98%) of compound **XIII**.

Bicyclic alcohols **XIV–XVIII** were prepared in the similar way; their characteristics are given in Table 4.

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