ISSN 1070-4280, Russian Journal of Organic Chemistry, 2010, Vol. 46, No. 5, pp. 628–630. © Pleiades Publishing, Ltd., 2010.
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# Synthesis of Bi- and Tricyclic Acrylates in the Presence of Boron Trifluoride Etherate

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Received May 31, 2009

**Abstract**—The addition of acrylic acid to bicyclo[2.2.1]heptene hydrocarbons and tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene catalyzed with $BF_3{\cdot}O(C_2H_5)_2$ was studied and bi- and tricyclic esters of acrylic acid were synthesized that were reactive monomers for preparation of macromolecular compounds.

**DOI:** 10.1134/S1070428010050039

Aliphatic and alicyclic esters of acrylic acids are successfully employed as reactive monomers in the synthesis of valuable polymers applied in the medicine [1, 2], cosmetic [3], electronic [4], and paint-and lacquer [5] industries.

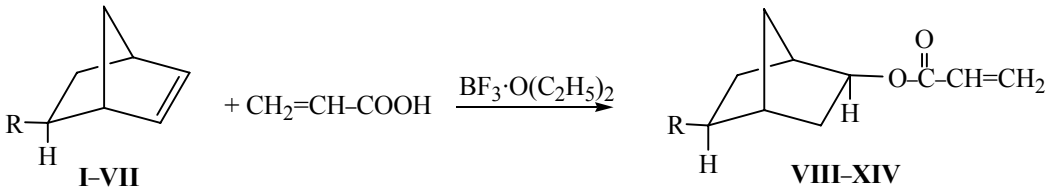
We formerly investigated the addition of (meth)acrylic acids to bi- and tricyclic olefin hydrocarbons in the presence as a catalyst of the ionexchanger KU-2-8, and also the thermal addition. Thus the corresponding esters were synthesized [6–9].

In this study we explored the reaction of the acrylic acid with bicycloolefin hydrocarbons **I–VII** catalyzed by boron trifluoride etherate $BF_3{\cdot}O(C_2H_5)_2$. The corresponding bicyclic esters **VIII–XIV** were synthesized (Scheme 1).

The acrylic acid like saturated mono- and dicarboxylic acids [10, 11] adds stereo- and regioselectively to bicyclo[2.2.1]-hept-2-ene with the formation of *exo*-2-bicyclic esters. The synthesized alkylbicycloalkyl acrylates according to the GLC analysis are composed of two regioisomers: 97–98% of *exo*-5-alkyl- and 2–3% of *exo*-6-alkyl-substituted esters.

The reaction of acrylic acid with tricyclo[5.2.1.$0^{2,6}$]-deca-3,8-diene (**XV**) was also studied. It added exclusively to the π-bond of the norbornene ring in the molecule of the tricyclic hydrocarbon leaving intact the double bond

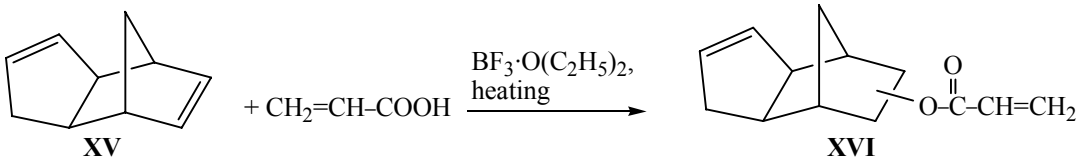
**Scheme 1.**




**I–VII** **VIII–XIV**

R = H (**I, VIII**), $CH_3$ (**II, IX**), $C_2H_5$ (**III, X**), *iso*-$C_3H_7$ (**IV, XI**), $C_3H_7$ (**V, XII**), $C_4H_9$ (**VI, XIII**), $C_5H_{11}$ (**VII, XIV**).

**Scheme 2.**




**XV** **XVI**

of cyclopentene. Two regioisomers formed as a result: tricyclo-[5.2.1.$0^{2,6}$]dec-3-en-8- and 9-yl esters with the first isomer largely prevailing (94–96%) (Scheme 2).

In order to developing the optimum conditions for the formation of bicyclo[2.2.1]hept-*exo*-2-yl acrylate we studied the dependence of the ester yield on the temperature, the molar ratio of reagents, amount of $BF_3{\cdot}O(C_2H_5)_2$ catalyst, and the reaction duration. The following reaction conditions were found to be optimum: temperature 80°C, molar ratio of initial compounds (**I**)–acrylic acid 1:1.2, quantity of the catalyst 0.5 wt%, reaction time 3 h. Yield of bicyclo[2.2.1]hept-*exo*-2-yl acrylate 80%. Under the found conditions the addition of acrylic acid to 5-alkylbicyclo[2.2.1]hept-2-enes **II–VIII** was carried out with the preparation of the corresponding esters in 65–77% yield.

Under the same conditions the addition of the acrylic acid to tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**XV**) in the presence of $BF_3{\cdot}O(C_2H_5)_2$ proceeded with the formation of tricyclo[5.2.1.$0^{2,6}$]dec-3-en-8(9)-yl acrylate (**XVI**) in 82% yield.

The purity, isomeric composition, and the structure of the acrylates synthesized were investigated and confirmed by GLC, IR and $^1$H, $^{13}$C NMR spectra, According to GLC the purity of esters obtained was 98–99%.

In the IR spectra of bi- and tricyclic acrylates alongside the strong absorption bands in the region 1735 (C=O) and 1070 cm$^{-1}$ (–COO–) characteristic of the ester group strong absorption bands appear in the region 810–890 cm$^{-1}$ corresponding to the vibrations of the terminal $CH_2$=CH group. In the IR spectrum of tricyclo-[5.2.1.$0^{2,6}$]dec-3-en-8(9)-yl acrylate (**XVI**) the absorption band in the region 1640 cm$^{-1}$ belongs to the stretching vibrations of the C=C bond in the cyclopentene ring.

The $^1$H NMR spectrum of compound **XVI** contains peaks in the region 5.75–6.23 ppm characteristic of the vinyl group. The signals of the *exo*-protons H$^2$ appear in the region 4.60–4.80 ppm.

The signals of the carbon atom of the carboxy group in the $^{13}$C NMR spectra are observed in the region 160.81–169.52 ppm, of the vinyl group carbon atoms, in the region 135.4–137.0 ppm.

Among the esters synthesized *exo*-bicyclo[2.2.1]-hept-2-yl acrylate (**VIII**) possesses a pleasant fruit scent and can be used as a component of synthetic fragrant substances. Compounds **VIII–XIV** and **XVI** are reactive monomers for preparation of macromolecular compounds.

## EXPERIMENTAL

The composition and the degree of purity of the synthesized mono- and diesters and also of the used initial compounds were checked by GLC. The GLC analysis was carried out on a chromatograph LKhM-8 MD, column length 1.5 m, stationary phase 10 wt% of poly(ethylene glycol) succinate on spherochrom, vaporizer temperature 200–250°C, oven temperature 120–150°C, carrier gas helium, flow rate 45 ml/min.

IR spectra were recorded on a spectrophotometer UR-20, $^1$H and $^{13}$C NMR spectra were registered on a spectrometer Tesla BS-487 C at operating frequency 80 MHz, internal reference HMDS, solvent $CCl_4$.

$^{13}$C NMR spectra of esters were taken on an instrument Varian at the frequency 80 MHz, solvent dioxane.

Initial cycloolefins had the following physicochemical constants: bicyclo[2.2.1]hept-2-ene (**I**), bp 96°C, mp 46°C; *exo*-5-methylbicyclo[2.2.1]hept-2-ene (**II**), bp 115°C, $d_4^{20}$ 0.8605, $n_D^{20}$ 1.4600; *exo*-5-ethylbicyclo[2.2.1]-hept-2-ene (**III**), bp 130–132°C, $d_4^{20}$ 0.8570, $n_D^{20}$ 1.4615; *exo*-5-iso-propylbicyclo[2.2.1]hept-2-ene (**IV**), bp 142°C, $d_4^{20}$ 0.8586, $n_D^{20}$ 1.4658; *exo*-5-propylbicyclo[2.2.1]-hept-2-ene (**V**), bp 147°C, $d_4^{20}$ 0.8608, $n_D^{20}$ 1.4662; *exo*-5-butylbicyclo[2.2.1]hept-2-ene (**VI**), bp 72°C (16 mm Hg), $d_4^{20}$ 0.8705, $n_D^{20}$ 1.4698; *exo*-5-amyl-bicyclo[2.2.1]hept-2-ene (**VII**), bp 96°C (20 mm Hg), $d_4^{20}$ 0.8706, $n_D^{20}$ 1.4702; they were obtained by procedure [12]; *exo*-tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**XV**), bp 170°C (decomp.), mp 19.5°C, $d_4^{20}$ 0.9760, $n_D^{20}$ 1.5051 [13].

The initial acrylic acid was a chemically pure substance with the physical constants identical to the published data [14]. Catalyst $BF_3{\cdot}O(C_2H_5)_2$, bp 126°C, $d_4^{20}$ 1.1540 [15].

The addition of the acrylic acid to cycloolefins was carried out in the alkylating installation equipped with a thermometer and a magnetic stirrer. On completion of the reaction $BF_3{\cdot}O(C_2H_5)_2$ catalyst was removed from the reaction mixture by washing with distilled water. The synthesized esters were separated from the reaction mixture by a vacuum distillation.

***exo*-Bicyclo[2.2.1]hept-2-yl acrylate (VIII)**. A mixture of 47 g of compound **I**, 43.2 g of acrylic acid, and 0.22 g of the catalyst was heated at 80°C. By the vacuum fractionation 66.4 g (80%) of compound **VIII** was isolated from the reaction mixture, bp 108–109°C (30 mm Hg), $d_4^{20}$ 1.0321, $n_D^{20}$ 1.4724. IR spectrum, cm$^{-1}$: 1730 (C=O), 1240–1245 (C–O–C), 815, 890 ($CH_2$=CH–).

$^1$H NMR spectrum, δ, ppm: 1.0–1.41 d (8H, 4$CH_2$), 2.20–2.22 m (2H, 2CH), 4.6 d (1H, CH), 5.75 t (2H, $CH_2$=), 6.23 d (1H, CH=). $^{13}$C NMR spectrum, δ, ppm: 28.08 ($C^5$), 29.6 ($C^7$), 35.45 ($C^6$), 35.92 ($C^4$), 40.0 ($C^3$), 42.12 ($C^1$), 77.31 ($C^2$), 135.6 ($C^{10}$), 137.0 ($C^9$), 168.6 ($C^8$). Found, %: C 72.22; H 8.80. $C_{10}H_{14}O_2$. Calculated, %: C 72.26; H 8.89.

***exo*-5-Methylbicyclo[2.2.1]hept-2-*exo*-yl acrylate (IX).** A mixture of 54 g of compound **II**, 43.2 g of acrylic acid, and 0.22 g of the catalyst was heated at 80°C. We isolated 68.9 g (77%) of compound **IX**, bp 117–118°C (30 mm Hg), $d_4^{20}$ 0.9968, $n_D^{20}$ 1.4769. $^1$H NMR spectrum, δ, ppm: 1.1 t (3H, $CH_3$), 1.10–1.44 d (6H, 3$CH_2$), 2.20–2.22 m (2H 2CH), 4.5–4.6 d (2H, 2CH), 5.75 t (2H, $CH_2$=), 6.23 d (1H, CH=). $^{13}$C NMR spectrum, δ, ppm: 28.08 ($C^5$), 28.4 ($C^{11}$), 29.6 ($C^7$), 35.45 ($C^6$), 35.92 ($C^4$), 40.00 ($C^3$), 42.12 ($C^1$), 77.31 ($C^2$), 135.4 ($C^{10}$), 137.0 ($C^9$), 168.3 ($C^8$). Found, %: C 73.26; H 8.89. $C_{11}H_{16}O_2$. Calculated, %: C 73.30; H 8.94.

***exo*-5-Ethylbicyclo[2.2.1]hept-2-*exo*-yl acrylate (X)**. From 61 g of compound **III**, 43.2 g of acrylic acid, and 0.22 g of the catalyst at 80°C we obtained 71.0 g (73%) of compound **X**, bp 136–137°C (30 mm Hg), $d_4^{20}$ 0.9866, $n_D^{20}$ 1.4783. Found, %: C 74.15; H 9.29. $C_{12}H_{18}O_2$. Calculated, %: C 74.19; H 9.33.

***exo*-5-Isopropylbicyclo[2.2.1]hept-2-*exo*-yl acrylate (XI).** A mixture of 68 g of compound **IV**, 43.2 g of acrylic acid, and 0.22 of the catalyst was heated at 80°C. We isolated 73.9 g (71%) of compound **XI**, bp: 142–143°C (30 mm Hg), $d_4^{20}$ 0.9700, $n_D^{20}$ 1.4790. Found, %: C 74.91; H 9.57. $C_{13}H_{20}O_2$. Calculated, %: C 74.96; H 9.67.

***exo*-5-Propylbicyclo[2.2.1]hept-2-*exo*-yl acrylate (XII).** From 68 g of compound **V**, 43.2 g of acrylic acid, and 0.22 g of the catalyst at 80°C we obtained 75.8 g (68%) of compound **XII**, bp 159–160°C (30 mm Hg), $d_4^{20}$ 0.9712, $n_D^{20}$ 1.4815. Found, %: C 74.92; H 9.61. $C_{13}H_{20}O_2$. Calculated, %: C 74.96; H 9.67.

***exo*-5-Butylbicyclo[2.2.1]hept-2-*exo*-yl acrylate (XIII).** A mixture of 75 g of compound **VI**, 43.2 g of acrylic acid, and 0.22 g of the catalyst was heated at 80°C. We isolated 74.3 g (67%) of compound **XIII**, bp 179–180°C (30 mm Hg), $d_4^{20}$ 0.9699, $n_D^{20}$ 1.4833. Found, %: C 75.60; H 9.95. $C_{14}H_{22}O_2$. Calculated, %: C 75.63; H 9.70.

***exo*-5-Amylbicyclo[2.2.1]hept-2-*exo*-yl acrylate (XIV).** A mixture of 82 g of compound **VII**, 43.2 g of acrylic acid and 0.22 g of the catalyst was heated at 80°C. We isolated 76.8 g (65%) of compound **XIV**, bp 192–193°C (30 mm Hg), $d_4^{20}$ 0.9678, $n_D^{20}$ 1.4867. Found, %: C 76.22; H 10.11. $C_{15}H_{24}O_2$. Calculated, %: C 76.27; H 10.16.

***exo*-Tricyclo[5.2.1.0$^{2,6}$]dec-3-en-8(9)-*exo*-yl acrylate (XVI).** From 66 g of compound **XV**, 36.0 g of acrylic acid, and 0.18 g of the catalysts at 80°C we obtained 83.6 g (82%) of compound **XVI**, bp 105–108°C (2 mm Hg), $d_4^{20}$ 1.0882, $n_D^{20}$ 1.5025. IR spectrum, ν, cm$^{-1}$: 1730 (C=O), 1300–1050 (C–O–C), 1640 (–CH=CH–), 810–890 ($CH_2$=CH–). $^1$H NMR spectrum, δ, ppm: 1.32 m (2H, $CH_2$), 1.32–2.14 m (4H, 2$CH_2$), 2.16 d (2H, 2CH), 2.46 d (2H, 2CH), 4.65 d (1H, CH), 5.55–5.60 q (2H, 2CH=), 5.75 t (2H, $CH_2$=), 6.23 d (1H, CH=). $^{13}$C NMR spectrum, δ, ppm: 182.1 ($C^{11}$), 137.0 ($C^{12}$), 135.6 ($C^{13}$), 47.3 ($C^1$), 46.1 ($C^2$), 134.2 ($C^3$), 131.0 ($C^4$), 41.8 ($C^5$), 44.0 ($C^6$), 47.0 ($C^7$), 59.7 ($C^8$), 49.5 ($C^9$), 32.0 ($C^{10}$). Found, %: C 76.42; H 7.83. $C_{13}H_{16}O_2$. Calculated, %: C 76.44; H 7.89.

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