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## BRIEF COMMUNICATIONS

# Synthesis of Halomethyl-Substituted Bicyclo[2.2.1]hept-2-yl(meth)acrylates

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**Abstract—**Bicyclic esters, which are reactive monomers for the synthesis of new polymeric products and also of organic compounds, were synthesized by the reaction of thermal addition of (met)acrylic acids to 5-halogen-substituted bicyclo[2.2.1]hept-2-en hydrocarbons in the presence of the inhibitor anthraquinone.

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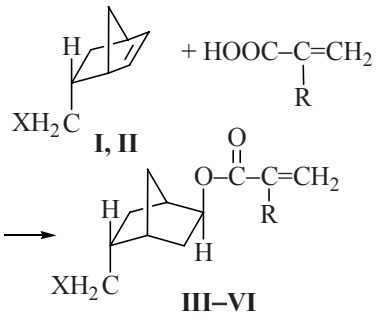
In recent years alkyl-and cycloalkyl (met)acrylic esters are successfully used as reactive monomers for obtaining practically valuable polymeric products which are applied as superglues, optical lenses, and paintwork materials [1–4].

Earlier effective procedures have been developed for the synthesis of alicyclic esters with a framework structure by thermal, and also catalytic addition of (met)acrylic acids to bi- and tricyclic olefin hydrocarbons [5–7] and for the preparation of practically valuable polymeric products of interest as paintwork materials on the basis of these esters [8].

To obtain the monomers, i.e. halogen-containing alicyclic acrylates of a framework structure adding to polymeric products such specific properties as flexibility and frost- and wear-resistance, we have studied the reaction of the thermal addition of acrylic acids to 5-halimethylsubstituted bicyclo[2.2.1]hept-2-en hydrocarbons:




X = Cl, R = H (**III**); X = Cl, R = $CH_3$ (**IV**); X = Br, R = H (**V**); X = Br, R = $CH_3$ (**VI**).

To prevent side oligomerization reactions of initial acrylic (AA) and methacrylic (MAA) acids, and also of resulting halomethylbicyclic esters of acrylates, we applied anthraquinone (AN) as an inhibitor. Unlike the known inhibitor hydroquinone this inhibitor in-creases the yield of target products (met)acrylates approximately by 15–22%. It results from the fact that in this reaction π-bonds of acrylic acids with anthraquinone form a stable quinhydrone-type intermediate complex [9].

To optimize reaction conditions, we have studied the effects of temperature, molar ratio of reacting components, using AA and 5-chloromethylbicyclo [2.2.1]-hept-2-en (CB) as an example, and reaction duration on the yield of 5-chlorometylbicyclo [2.2.1] hept-2-ylacrilate (CBA). The results of these studies have shown that the optimal conditions of the reaction are as follows: temperature 120°C, duration 3 h, ratio of the initial components CB:AA=1:1.2 (mol), and AN content 0.01% to an AA weight. Under these conditions the thermal addition of MAA to CB was studied, and 5-chloromethylbicyclo[2.2.1]hept-2-ylmethacrylate (CBMAC) was synthesized.

It was found that the optimal conditions for the reaction of AA and MAA addition to 5-bromomethylbicyclo-[2.2.1] hept-2-en (BB) are the same as for the reaction of the CBA synthesis. The results of the synthesis of halogen-containing bicyclic (met)acrylates under optimal conditions are given in Table 1.

**Table 1.** Conditions of the reaction of CB and BB with AA and MAA

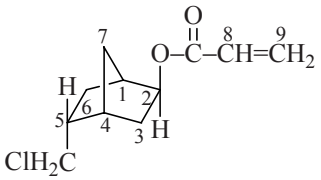
| Taken, g | | | | Expermental conditions | | Obtained | |
|---|---|---|---|---|---|---|---|
| CB | BB | AA | MAA | $T$, °C | τ, h | Comp. no. | g |
| 142.5 | – | 86.4 | – | 120 | 3 | **III** | 173.8 |
| 142.5 | – | – | 103.2 | 120 | 3 | **IV** | 171.4 |
| – | 187 | 86.4 | – | 120 | 3 | **V** | 230.5 |
| – | 187 | – | 103.2 | 120 | 3 | **VI** | 224.13 |

The purity of the synthesized (met)acrylates determined by gas-liquid chromatography was 99–99.3%. The resulting esters consist of two stereoisomers: 92-95% of *endo*-5-halomethylbicyclo[2.2.1] hept-*exo*-2-ylacrilates and 5-8% of *exo*-5-halomethylbicyclo-[2.2.1]hept-*exo*-2-yl(met)acrylates. The physicochemical constants of the synthesized esters are given in Table 2.

The signals at 820 and 890 $cm^{-1}$ in combination with the band at 1640 $cm^{-1}$ in the IR spectra of the synthesized halogen-containing bicyclic acrylates point to the presence of a vinyl group in the molecules, the absorption bands at 1720–1730 and 1240–1245 $cm^{-1}$ prove the presence of an ester group –C(O)–O–, and at 1380 $cm^{-1}$, of a methyl group. The strong band in the region of 990–1000 $cm^{-1}$ in the spectra proves the presence of the *exo*-isomer of (met)acrylates.

Protons of the $ClCH_2$ group in the NMR spectra of chloromethylbicyclic esters appear in the region of 3.70 ppm, and those of the $BrCH_2$ group, in the region of 4.10 ppm. The chemical shift of hydrogen at the second carbon atom in the region of 4.60 ppm proves its *exo*-position. The chemical shifts 5.70–6.25 ppm point to the presence of a vinyl group in the synthesized acrylates, the CH- and $CH_2$ groups in the esters are observed in the region of 1.0–2.20 ppm.

Below the IR spectrum and the $^1H$ NMR chemical shifts of *endo*-5-chloromethylbicyclo[2.2.1]hept-*exo*-2-ylacrilate are given as an example:




$^1H$ NMR, ppm: 2.20 (1), 4.60 (2), 1.45 (3), 2.22 (4), 1.50 (5), 1.31 (6), 1.35 (7), 6.20 (8), 5.70 (9), 5.70 (10).

**Table 2.** Physicochemical constants and yield of halogenmethyl-substituted bicyclic (met)acrylates

| Comp. no. | bp, °C ($p$, mm Hg) | $d_4^{20}$ | $n_D^{20}$ | Yield, % |
|---|---|---|---|---|
| **III** | 108–111/2.5 | 1.1637 | 1.4716 | 81.0 |
| **IV** | 106–109/1.2 | 1.1580 | 1.4799 | 75.0 |
| **V** | 112–114/1.2 | 1.2482 | 1.4740 | 89.0 |
| **VI** | 124–127/1.2 | 1.2067 | 1.4779 | 82.0 |

IR, γ, $cm^{-1}$: 1000–890 ($CH_2$=CH–), 1730 (C=O), 1300–1065 (–O–), 730 (Cl–$CH_2$–), 1645 (C=C), 1415, 2910, 3000 (CH–, $CH_2$–).

Synthesized (met)acrylates have a specific odor, they are transparent liquids readily polymerized on storage to form a transparent vitreous polymeric compound. In view of this fact we can assume that the synthesized halogen-containing (met)acrylates are new reactive monomers feasible for the preparation of high-molecular compounds.

## EXPERIMENTAL

The purity and composition of synthesized halogen-containing bicyclic (met)acrylates were determined by gas-liquid chromatography on an LKhM-8 MD instrument; the length of a column 1.5 m; stationary phase: 10% polyethyleneglycol succinate on spherochromium; the temperature of evaporator, column, and detector were 200, 120, and 100°C, respectively; the rate of gas-carrier 45 ml $min^{-1}$.

The IR spectra were taken on a UR-20 instrument in $CCl_4$; the $^1H$ NMR spectra on a Tesla BS-487 C instrument at the operating frequency of 80 MHz at 20°C, internal reference HMDS, measurement accuracy δ = 0.05 ppm.

The reaction of AA and MAA addition to halogen-containing bicyclic hept-2-en hydrocarbons was carried out in an ampoule made of stainless steel.

The used initial compounds had the following physicochemical constants: CB: mp 50.5–51.5°C (9 mm Hg) $d_4^{20}$ = 1.0651, $n_D^{20}$ 1.4450 [10]; BB: mp 67–68°C (9 mm Hg) $d_4^{20}$ = 1.3715, $n_D^{20}$ 1.5211 [10]; mp 141°C, $n_D^{20}$ = 1.062, $n_D^{20}$ = 1.4224 [11]; MAA: mp 160.5°C, $n_D^{20}$ = 1.015, $n_D^{20}$ = 1.4314 [11]; AN: bp 379–381°C, mp 286°C [11].

The initial compounds and AN were loaded in the ampoule, hermetically closed, and heated in a thermostat at 120°C for 3 h. After completion of the heating the ampoule was cooled to room temperature, its content was subjected to vacuum distillation, and a target product was isolated with a yield of 75–89%.

The synthesized (met)acrylates are of interest as initial compounds for the synthesis of various organic products and also can be applied as insecticides.

## CONCLUSIONS

(1) 5-halogenmethylbicyclo[2.2.1]hept-2-yl esters were synthesized with a yield of 75–89% by the thermal addition of acrylic and methacrylic acids to 5-halogenmethylbicyclo[2.2.1]-hept-2-en.

(2) It was found that the thermal addition of acrylic acids to halogenmethylbicyclo[2.2.1]-hept-2-en results in the formation of *exo*-isomers.

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