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# Synthesis of Esters by Addition of Chloroacetic Acid to Cage-Like Cyclic Olefins

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**Abstract**—Thermal addition of chloroacetic acid to bicyclo[2.2.1]hept-2-ene, its 5-alkyl-substituted derivatives, and tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene gave the corresponding chloroacetic acid esters which attract interest as potential insecticides for plant protection.

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We previously studied addition of saturated aliphatic acids to cage-like bi- and tricyclic unsaturated hydrocarbons and thus synthesized various esters [1–3], including 5-methylnorbornyl acetate (Menorate) and tricyclo[5.2.1.$0^{2,6}$]dec-3-en-8(9)-yl acetate (Dicylate) which possess a pleasant odor and are used in perfumery as components of fragrant substances [4, 5]. Addition of acrylic acids to bi- and tricyclic olefins gives reactive monomers [6, 7]. It is known that alkyl and cycloalkyl esters derived from chlorine-containing acids are also effective insecticides [8] and agents preventing corrosion of petroleum pipelines [9].

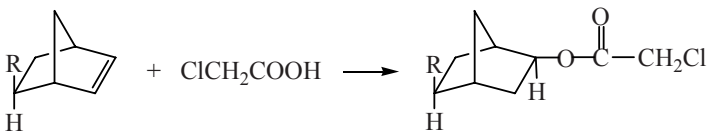
Taking into account practical importance of chlorinated esters, we have found that the most efficient procedure for their preparation is addition of chloroacetic acid to cage-like cyclic olefins (Scheme 1).

The results of our studies have demonstrated that chloroacetic acid stereoselectively adds at the double bond of bicyclo[2.2.1]hept-2-ene on heating to give bicyclo[2.2.1]hept-*exo*-2-yl chloroacetate. According to the chromatographic analysis data, esters obtained from 5-alkylbicyclo[2.2.1]hept-2-enes are mixtures of two regioisomers, each having *exo* configuration (the initial 5-alkylbicyclo[2.2.1]hept-2-enes were *exo* isomers). The ratio of 6- and 5-alkyl-substituted isomers changed from 4:96 to 10:90. The purity of the isolated chloroacetic acid esters was 99.0–99.5%, and their structure was proved by the IR and $^1$H NMR spectra. The yield of the chloroacetic acid esters decreased as the length of the alkyl radical in the initial 5-alkylbicyclo[2.2.1]hept-2-enes increased (H > Me > Et > *n*-Pr > *n*-Bu > *n*-$C_5H_{11}$; see table). Presumably, alkyl radicals reduce the reactivity of the double C=C bond in molecules of bicycloheptene hydrocarbons.

We were also interested in synthesizing tricyclic chlorine-containing esters. For this purpose, we examined addition of chloroacetic acid to tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**XIII**); the reaction gave tricyclo[5.2.1.$0^{2,6}$]dec-3-en-8(9)-yl chloroacetate **XIV**. (Scheme 2)

Like initial olefin **XIII** (mp 19.5°C), compound **XIV** had *exo*,*exo* configuration, the ratio of regioisomers **XIV** and **XIVA** was 97:3%, and the purity was 98.9–99.1% according to the GLC data (Scheme 3).

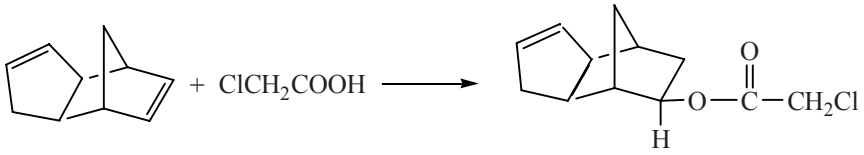
**Scheme 1.**




**I–VI** **VII–XII**

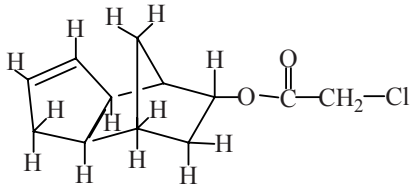
**I**, **VII**, R = H; **II**, **VIII**, R = Me; **III**, **IX**, R = Et; **IV**, **X**, R = *n*-Pr; **V**, **XI**, R = *n*-Bu; **VI**, **XII**, *n*-$C_5H_{11}$.

**Scheme 2.**




**XIII** **XIV**

**Scheme 3.**




**XIVA**

The IR spectra of esters **VII–XII** and **XIV** contained strong absorption bands in the regions 1765 and 1050–1300 $cm^{-1}$ due to stretching vibrations of the ester carbonyl and C–O–C groups, respectively. Tricyclic ester **XIV** displayed in the IR spectrum an additional absorption band at 1640 $cm^{-1}$, belonging to stretching vibrations of the C=C bond. In the $^1H$ NMR spectra of these compounds, signals from the *exo*-oriented protons on $C^2$ and $C^5$ in the bicyclic skeleton appeared at δ 4.80 and 4.90 ppm, and the $ClCH_2$ protons resonated at δ 4.38 ppm. The structure of ester **VII** (R = H) was also proved by independent synthesis, esterification of bicyclo[2.2.1]hept-*exo*-2-ol with chloroacetic acid in the presence of naphthalene-1,5-disulfonic acid. The yields, boiling points, densities, refractive indices, and elemental analyses of compounds **VII–XII** and **XIV** are given in table.

Preliminary tests showed that some of the synthesized chloroacetic acid esters exhibit strong insecticidal activity.

## EXPERIMENTAL

The purity of the products was checked by GLC on an LKhM-8MD chromatograph; 1.2–1.5-m column packed with 10% of polyethylene glycol succinate on Sferokhrom; injector temperature 140°C, oven temperature 120°C, detector temperature 250°C; detector current 120 mA; carrier gas helium, flow rate 45 ml/min. The IR spectra were recorded on a UR-20 spectrometer. The $^1H$ NMR spectra were measured on a Tesla BS-487C spectrometer (Czech Republic) at 80 MHz using carbon tetrachloride as solvent and hexamethyldisiloxane as internal reference.

Initial bicyclo[2.2.1]heptenes **I–VI** were synthesized as mixtures of *endo* and *exo* isomers by Diels–Alder reaction of cyclopentadiene with the corresponding olefins [10, 11]. The *endo* isomers were converted into the *exo* isomers by heating for 3 h at 200°C in a steel ampule. Below are listed the parameters of the *exo* isomers of **I–VI** and **XIII**:

Yields, physical constants, and elemental analyses of chloroacetic acid esters **VII–XII** and **XIV**

| Comp. no. | Yield, % | bp, °C (2 mm) | $d_4^{20}$ | $n_D^{20}$ | Found, % | | | Formula | Calculated, % | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | Cl | | C | H | Cl |
| **VII** | 95.5 | 83–84 | 1.1731 | 1.4826 | 57.11 | 6.32 | 18.71 | $C_9H_{13}O_2Cl$ | 57.30 | 6.41 | 18.79 |
| **VIII** | 90.4 | 92–93 | 1.1392 | 1.4836 | 59.00 | 7.10 | 17.21 | $C_{10}H_{15}O_2Cl$ | 59.26 | 7.46 | 17.49 |
| **IX** | 89.1 | 107–108 | 1.1211 | 1.4841 | 60.66 | 7.65 | 16.01 | $C_{11}H_{17}O_2Cl$ | 60.97 | 7.91 | 16.39 |
| **X** | 86.5 | 108–109 | 1.1195 | 1.4856 | 62.14 | 8.13 | 15.00 | $C_{12}H_{19}O_2Cl$ | 62.47 | 8.30 | 15.37 |
| **XI** | 85.0 | 126–127 | 1.1136 | 1.4962 | 63.58 | 8.51 | 14.20 | $C_{13}H_{21}O_2Cl$ | 63.79 | 8.65 | 14.48 |
| **XII** | 84.1 | 137–138 | 1.1102 | 1.4871 | 64.87 | 8.90 | 13.51 | $C_{14}H_{23}O_2Cl$ | 64.98 | 8.96 | 13.70 |
| **XIV** | 96.0 | 119–121 | 1.1801 | 1.5165 | 63.41 | 6.56 | 15.41 | $C_{12}H_{15}O_2Cl$ | 63.58 | 6.67 | 15.64 |

bicyclo[2.2.1]hept-2-ene (**I**): bp 96°C, mp 46°C, purity 99.8% (GLC); *exo*-5-methylbicyclo[2.2.1]-hept-2-ene (**II**): bp 115.5°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, purity 98.7%; *exo*-5-propylbicyclo[2.2.1]hept-2-ene (**IV**): bp 147°C, $d_4^{20}$ = 0.8604, $n_D^{20}$ = 1.4668; *exo*-5-butylbicyclo[2.2.1]hept-2-ene (**V**): bp 72°C (16 mm), $d_4^{20}$ = 0.8705, $n_D^{20}$ = 1.4698; *eco*-5-pentylbicyclo[2.2.1]hept-2-ene (**VI**): bp 96°C (20 mm), $d_4^{20}$ = 0.8706, $n_D^{20}$ = 1.4702; *exo*-tricyclo [5.2.1.$0^{2,6}$]deca-3,8-diene (**XIII**): bp 160°C (decomp.), mp 19.5°C, $d_4^{20}$ = 0.9760, $n_D^{20}$ = 1.5050, purity 99.5% [12]. Chloroacetic acid had bp 189°C, $d_4^{20}$ = 1.5800.

**Chloroacetic acid esters VII–XII and XIV (***general procedure***).** A mixture of 0.5 mol of cage-like olefin **I–VI** or **XIII** and 0.5 mol of chloroacetic acid was heated for 3 h at 110°C. The unreacted initial compounds were removed by fractional distillation, and esters **VII–XII** and **XIV** were isolated by vacuum distillation.

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