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Synthesis and Biological Activity of Permethrinic Acid Analogs Containing Various Substituents in Position *2* of the Cyclopropane Ring

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Abstract—A number of permethrinic acid ethyl ester derivatives having various substituents [Et, Pr, Ph, $Ph(CH_2)_n$ (n = 1, 2), etc.] in position *2* of the cyclopropane ring were synthesized, and their insecticidal acivity against typhoid flies, rice weevils, and bean aphides, as well as juvenoid activity on flour beetle chrysalises, was studied. The newly synthesized compounds turned out to exhibit weak insecticidal activity against standard insects but pronounced juvenile hormone activity, which differentiates them from permethrinic acid esters.

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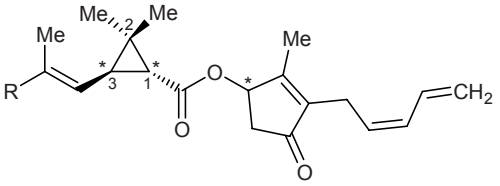
Pyrethroids are analogs of naturally occurring pyrethrins (**A**) that are esters derived from substituted cyclopropanecarboxylic acid; these compounds are isolated from flowers of some *Chrysanthemum* species, and they exhibit insecticidal activity.



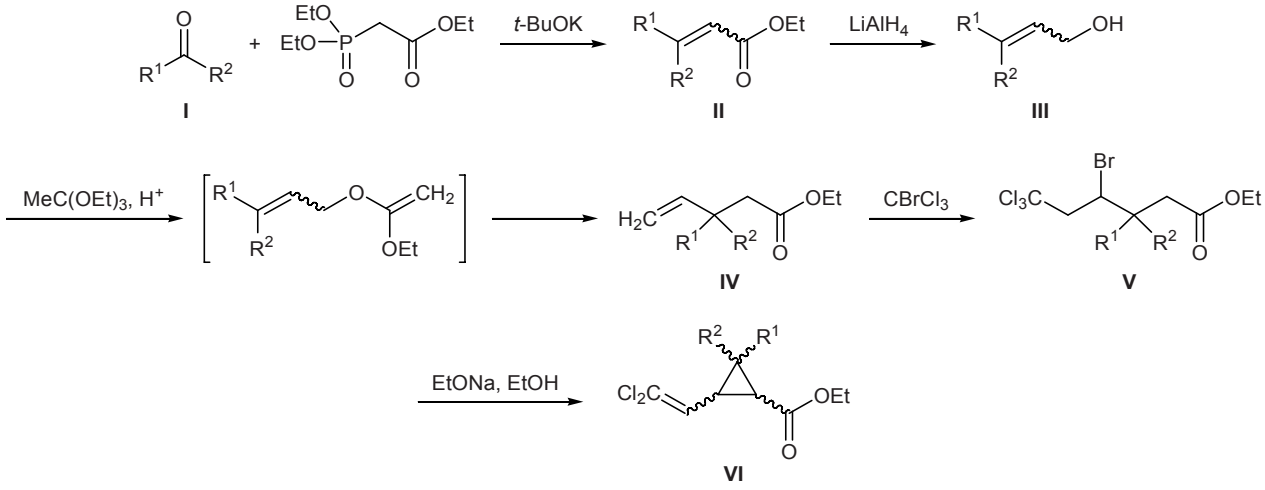
A

R = Me, MeOCO.

Published data on the synthesis and properties of pyrethroids [1–5] indicate that all cyclopropanecarboxylic acid derivatives possessing strong insecticidal activity have a common structural fragment, namely geminal methyl groups in position *2* of the cyclopropane ring. The role of this structural fragment has not been clearly understood. It was presumed that the geminal methyl groups maintain spatial configuration of the cyclopropane moiety in active molecules [2]. Both methyl groups are likely to be responsible for biological activity of pyrethroids, for all known derivatives having no methyl groups are inactive [6]. On the other hand, the possibility for obtaining biologically active pyrethroid structures with different functional substituents in position *2* of the cyclopropane fragment (trifluoromethyl, cyano, phenyl) was noted in some publications [7–11].

With the goal of studying the structure–activity relations in the series of cyclopropanecarboxylic acid esters we synthesized permethrinic acid ethyl ester [ethyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-1-carboxylate] analogs containing various substituents (alkyl and aralkyl groups) in position *2* of the cyclopropane ring. For this purpose, ketones **I** were brought into reaction with ethyl (diethoxyphosphoryl)acetate to obtain substituted acrylic acid ethyl esters **II** [12] (Scheme 1). Selective reduction of the ester group in **II** with lithium tetrahydridoaluminate [13] gave the corresponding unsaturated alcohols **III** which were acylated with triethyl orthoacetate; the reaction involved Claisen-type rearrangement of intermediate acetal to give ethyl pent-4-enoates **IV** [14]. Catalytic addition of bromotrichloromethane at the double bond of esters **IV** resulted in the formation of ethyl 4-bromo-6,6,6-trichlorohexanoates **V**. Finally, dehydrohalogenation and cyclization of esters **V** by the action of ethanolic sodium ethoxide afforded the desired ethyl 2,2-disubstituted 3-(2,2-dichlorovinyl)cyclopropane-1-carboxylates **VI**.

Scheme 1.



R^1, R^2 = Me, Et, Pr, Ph, $PhCH_2$, $PhCH_2CH_2$; $R^1R^2 = (CH_2)_n$, n = 4, 5.

The products were isolated from reaction mixtures by standard procedures, including vacuum distillation, crystallization, and chromatographic separation using silica gel columns. The structure and purity of the isolated compounds were determined using various analytical methods, such as thin-layer, liquid, and gas–liquid chromatography, NMR spectroscopy, and mass spectrometry.

The structure of permethrinic acid ethyl ester analogs **VI** was studied using one- and two-dimensional NMR techniques (1H, ^{13}C, DEPT, ^1H 2D-COSY, ^1H–^{13}C 2D-CHCORR, ^1H 2D-ROESY) [15, 16]. We thus succeeded in assigning proton and carbon signals to particular isomers. Stereoisomers of compounds possessing two chiral centers were traditionally denoted as *cis* and *trans*. In compounds having three chiral centers, the ester group was selected as reference, and orientation of the other substituents with respect to the ester group was denoted by prefixes "*c*" and "*t*" [17]. The ^1H and ^{13}C NMR spectra of stereoisomers of compounds **VIa**–**VIk** are given in Experimental.* The relations holding in the ^1H and ^{13}C chemical shifts of substituents in the cyclopropane ring, located *cis* and *trans* with respect to the ester group, were described by us previously [18].

The isolated permethrinic acid ethyl ester analogs were tested for enteric, systemic, and juvenile activity in model insects (sensitive laboratory populations belonging to different systematic groups) and for acaricidal activity in sensitive laboratory mites. The screening was performed using threshold concentrations determined for each kind of activity and each systematic group of insects and mites [19, 20]. The results showed that replacement of two geminal methyl groups in position *2* of the cyclopropane ring by other alkyl, cycloalkyl, or ω-phenylalkyl groups leads to compounds possessing a weak insecticidal activity against test insects as compared to permethrinic acid ethyl ester taken as reference. On the other hand, unlike the latter, the examined compounds turned out to exhibit pronounced juvenile hormone activity (score 5–7 according to Schmialek). The compounds also showed weak phytotoxicity against plant leaves.

EXPERIMENTAL

The NMR spectra were recorded on a Bruker Avance-300 spectrometer at 300 MHz using $CDCl_3$ as solvent and tetramethylsilane as internal reference. The IR spectra were measured on a Perkin–Elmer 1720 spectrometer from solutions in carbon tetrachloride or neat substances (film). The mass spectra (electron impact) were obtained on a Fisons Trio 1000 GC–MS system (quadrupole mass analyzer; SPB-1 capillary column, 25 m×0.2 mm, stationary phase SE-54, film thickness 0.35 μm; carrier gas helium). Gas–liquid chromatography was performed on a Varian 3900 gas chromatograph equipped with a flame-ionization detector and a 15-m WCOT fused silica capillary column (injector temperature 200°C, detector temperature 220°C; split ratio 100, flow rate 1 ml/min, carrier gas nitrogen, 25 ml/min; hydrogen glow rate 25 ml/min, air flow rate 300 ml/min). HPLC analysis was per-

* The complete NMR spectra of the newly synthesized compounds are available from the authors by *e-mail*: *nsm21@yandex.ru*.

formed on a Millikhrom AO-2 liquid chromatograph equipped with a spectrophotometric detector and a C18 reversed-phase column; eluents: A (aqueous phase): 90% buffer (100 ml of distilled water, 0.2 ml of 10% trimethylamine, and 100 μg of heptanesulfonic acid) + 10% acetonitrile or distilled water without ionogenic compounds (constant pH value); B (organic phase): 90% acetonitrile + 10% distilled water; the eluent composition was programmed in a gradient mode (50 to 80% in 25 min, followed by keeping for 15 min). The progress of reactions was monitored by TLC on Silica gel 60 F254 plates (Merck) using hexane–benzene (1 : 1) or benzene–diethyl ether (9 : 1) as eluent; spots were visualized under UV light or by treatment with a solution of phosphomolybdic acid. Ethyl 4-bromo-6,6,6-trichlorohexanoates **V** and ethyl cyclopropanecarboxylates **VI** were isolated from the reaction mixtures by column chromatography on silica gel 60 (0.040–0.063 mm; Merck) using Kontes glass columns (300×48 mm i.d.).

Initial ketones **I**, 2-phenylethanol, 4-phenylbutan-2-one, ethyl (diethoxyphosphoryl)acetate, triethyl orthoacetate, bromotrichloromethane, 2-aminoethanol, potassium *tert*-butoxide, lithium tetrahydridoaluminate, copper(I) chloride, and sodium ethoxide were commercial products. Diethyl ether, benzene, *tert*-butyl alcohol, hexane, and phenol were purified by standard procedures [21]. Ethanol was dehydrated according to the procedure described in [13].

Ethyl β,β-substituted acrylates IIa–IIk (*general procedure*). Potassium *tert*-butoxide, 170 mmol, was added in portions under vigorous stirring to a mixture of 150 ml of anhydrous benzene, 140 mmol of ethyl (diethoxyphosphoryl)acetate, and 140 mmol of the corresponding ketone **I**, maintaining the temperature of the reaction mixture not exceeding 25–30°C. The mixture was stirred for 10–12 h at room temperature and poured into a beaker containing crushed ice. When the ice melted, the mixture was transferred into a separatory funnel, the upper organic layer was separated, washed with distilled water (2×50 ml), and dried over magnesium sulfate, the solvent was distilled off under reduced pressure on a rotary evaporator, and the residue was distilled in a vacuum (1–2 mm). The concentration of the main substance in the product was determined by HPLC.

Ethyl 3-ethylpent-2-enoate (IIa). Yield 54%, bp 63–67°C (3–4 mm), n_D^{20} = 1.4423, purity 98%. IR spectrum, ν, cm^{-1}: 1734 (C=O), 1675 (C=C). ^1H NMR spectrum, δ, ppm: 0.83 t (6H, CH_3), 1.10 t (3H, CH_3), 2.01 q (2H, CH_2), 2.43 q (2H, CH_2), 3.97 q (2H, CH_2O), 5.41 s (1H, CH=). Found, %: C 69.51; H 10.34. $C_9H_{16}O_2$. Calculated, %: C 69.23; H 10.25.

Ethyl 3-methylhex-2-enoate (IIb). Yield 67%, bp 56–63°C (1–2 mm), n_D^{20} = 1.4420, purity 98%. IR spectrum, ν, cm^{-1}: 1732 (C=O), 1670 (C=C). ^1H NMR spectrum, δ, ppm: 0.81 t (3H, CH_3), 1.23 t (3H, CH_3), 1.61 s (3H, CH_3), 1.85 m (2H, CH_2), 2.07 t (2H, CH_2), 3.87 q (2H, CH_2O), 5.23 s (1H, CH=). Found, %: C 69.51; H 10.34. $C_9H_{16}O_2$. Calculated, %: C 69.23; H 10.25.

Ethyl 3-propylhex-2-enoate (IIc). Yield 54%, bp 78–79°C (1–2 mm), n_D^{20} = 1.4419, purity 94%. IR spectrum, ν, cm^{-1}: 1730 (C=O), 1670 (C=C). ^1H NMR spectrum, δ, ppm: 0.81 t (6H, CH_3), 1.22 t (3H, CH_3), 1.87 m (4H, CH_2), 2.04 m (4H, CH_2), 3.91 q (2H, CH_2O), 5.33 s (1H, CH=). Found, %: C 71.96; H 10.54. $C_{11}H_{20}O_2$. Calculated, %: C 71.73; H 10.86.

Ethyl 3-ethylhex-2-enoate (IId). Yield 76%, bp 59–60°C (1–2 mm), n_D^{20} = 1.4431, purity 97%. IR spectrum, ν, cm^{-1}: 1735 (C=O), 1671 (C=C). ^1H NMR spectrum, δ, ppm: 0.90 t (6H, CH_3), 1.27 t (3H, CH_3), 1.57 m (2H, CH_2), 1.96 m (2H, CH_2), 2.42 m (2H, CH_2), 3.93 q (2H, CH_2O), 5.42 d (1H, CH=). Found, %: C 71.83; H 10.24. $C_{10}H_{18}O_2$. Calculated, %: C 70.58; H 10.58.

Ethyl 3-methylpent-2-enoate (IIe). Yield 55%, bp 53–55°C (3–4 mm), n_D^{20} = 1.4421, purity 96%. IR spectrum, ν, cm^{-1}: 1734 (C=O), 1672 (C=C). ^1H NMR spectrum, δ, ppm: 0.94 t (3H, CH_3), 1.14 t (3H, CH_3), 1.85 s (3H, CH_3), 2.02 m (2H, CH_2), 3.95 q (2H, CH_2O), 5.47 s (1H, CH=). Found, %: C 67.81; H 9.45. $C_8H_{14}O_2$. Calculated, %: C 67.60; H 9.85.

Ethyl cyclopentylideneacetate (IIf). Yield 56%, bp 200–201°C (760 mm), n_D^{20} = 1.4691, purity 90%. IR spectrum, ν, cm^{-1}: 1730 (C=O), 1670 (C=C). ^1H NMR spectrum, δ, ppm: 1.10 t (3H, CH_3), 1.65 m (4H, CH_2), 2.31 t (2H, CH_2), 2.63 t (2H, CH_2), 4.03 q (2H, CH_2O), 5.52 m (1H, CH=). Found, %: C 70.51; H 9.34. $C_9H_{14}O_2$. Calculated, %: C 70.12; H 9.09.

Ethyl cyclohexylideneacetate (IIg). Yield 86%, bp 92–95°C (3–4 mm), n_D^{20} = 1.4771, purity 98%. IR spectrum, ν, cm^{-1}: 1735 (C=O), 1670 (C=C). ^1H NMR spectrum, δ, ppm: 1.06 t (3H, CH_3), 1.50 m (6H, CH_2), 2.27 t (2H, CH_2), 2.58 t (2H, CH_2), 3.91 q (2H, CH_2O), 5.61 m (1H, CH=). Found, %: C 71.85; H 9.74. $C_{10}H_{16}O_2$. Calculated, %: C 71.42; H 9.52.

Ethyl 3-methyl-4-phenylbut-2-enoate (IIh). Yield 82%, bp 103–105°C (1–2 mm), n_D^{20} = 1.5140, purity

93%. IR spectrum, ν, cm^{-1}: 1734 (C=O), 1675 (C=C). ^1H NMR spectrum, δ, ppm: 1.05 t (3H, CH_3), 2.01 s (3H, CH_3), 3.15 s (2H, CH_2), 3.95 q (2H, CH_2O), 5.51 s (1H, CH=), 7.05 m (5H, C_6H_5). Found, %: C 76.85; H 7.54. $C_{13}H_{16}O_2$. Calculated, %: C 76.47; H 7.84.

Ethyl 3-benzylpent-2-enoate (IIi). Yield 65%, bp 115–117°C (1–2 mm), n_D^{20} = 1.5143, purity 96%. IR spectrum, ν, cm^{-1}: 1735 (C=O), 1674 (C=C). ^1H NMR spectrum, δ, ppm: 0.84 t (3H, CH_3), 1.02 t (3H, CH_3), 2.03 q (2H, CH_2), 3.12 s (2H, CH_2), 3.92 m (2H, CH_2O), 5.51 s (1H, CH=), 7.03 m (5H, C_6H_5). Found, %: C 76.35; H 8.52. $C_{14}H_{18}O_2$. Calculated, %: C 77.06; H 8.25.

Ethyl 3-methyl-5-phenylpent-2-enoate (IIj). Yield 76%, bp 114–116°C (1–2 mm), n_D^{20} = 1.5130, purity 96%. IR spectrum, ν, cm^{-1}: 1734 (C=O), 1672 (C=C). ^1H NMR spectrum, δ, ppm: 0.99 t (3H, CH_3), 1.82 s (3H, CH_3), 2.31 m (4H, CH_2), 3.69 q (2H, CH_2O), 5.23 s (1H, CH=), 6.92 s (5H, C_6H_5). Found, %: C 76.41; H 8.44. $C_{14}H_{18}O_2$. Calculated, %: C 77.06; H 8.25.

Ethyl 3-phenylbut-2-enoate (IIk). Yield 63%, bp 111–112°C (1–2 mm), n_D^{20} = 1.5255, purity 95%. IR spectrum, ν, cm^{-1}: 1735 (C=O), 1671 (C=C). ^1H NMR spectrum, δ, ppm: 1.27 t (3H, CH_3), 2.53 s (3H, CH_3), 4.45 q (2H, CH_2O), 4.52 t (1H, CH=), 7.15–7.25 m (5H, C_6H_5). Found, %: C 76.04; H 7.74. $C_{12}H_{14}O_2$. Calculated, %: C 75.78; H 7.36.

Substituted alkenols IIIa–IIIk (*general procedure*). A solution of 50 mmol of ester **IIa**–**IIk** in 50 ml of anhydrous diethyl ether was added under stirring to a suspension of 30 mmol of $LiAlH_4$ in 50 ml of anhydrous diethyl ether; the rate of addition was selected so that to maintain the mixture weakly boiling. The mixture was stirred for 4 h at room temperature, cooled with ice water, and 100 ml of 10% sulfuric acid was added dropwise to decompose excess reducing agent (until the precipitate dissolved completely). The product was extracted into diethyl ether (3×100 ml), the combined extracts were dried over magnesium sulfate, the solvent was distilled off under reduced pressure, and the residue was subjected to vacuum distillation. The concentration of the main substance in the product was determined by HPLC.

3-Ethylpent-2-en-1-ol (IIIa). Yield 76%, bp 55–56°C (1–2 mm), n_D^{20} = 1.4516, purity 99%. IR spectrum, ν, cm^{-1}: 3335 (OH), 1665 (C=C). ^1H NMR spectrum, δ, ppm: 0.85 m (6H, CH_3), 1.93 q (2H, CH_2), 2.06 q (2H, CH_2), 3.48 s (1H, OH), 4.13 d (2H, CH_2O), 5.22 m (1H, CH=). Found, %: C 73.24; H 12.34. $C_7H_{14}O$. Calculated, %: C 73.68; H 12.28.

3-Methylhex-2-en-1-ol (IIIb). Yield 81%, bp 69–70°C (1–2 mm), n_D^{20} = 1.4495, purity 94%. IR spectrum, ν, cm^{-1}: 3339 (OH), 1665 (C=C). ^1H NMR spectrum, δ, ppm: 0.96 t (3H, CH_3), 1.61 m (2H, CH_2), 2.02 s (3H, CH_3), 2.37 m (2H, CH_2), 3.75 s (1H, OH), 3.97 d (2H, CH_2O), 5.37 m (1H, CH=). Found, %: C 73.88; H 12.52. $C_7H_{14}O$. Calculated, %: C 73.68; H 12.28.

3-Propylhex-2-en-1-ol (IIIc). Yield 81%, bp 68–69°C (1–2 mm), n_D^{20} = 1.4534, purity 97%. IR spectrum, ν, cm^{-1}: 3338 (OH), 1664 (C=C). ^1H NMR spectrum, δ, ppm: 0.86 m (6H, CH_3), 1.51 m (2H, CH_2), 1.85 m (2H, CH_2), 2.15 m (2H, CH_2), 2.31 m (2H, CH_2), 3.21 s (1H, OH), 4.08 d (2H, CH_2O), 4.81 d.d (1H, CH=). Found, %: C 76.46; H 12.32. $C_9H_{18}O$. Calculated, %: C 76.05; H 12.67.

3-Ethylhex-2-en-1-ol (IIId). Yield 85%, bp 62–63°C (1–2 mm), n_D^{20} = 1.4524, purity 98%. IR spectrum, ν, cm^{-1}: 3338 (OH), 1665 (C=C). ^1H NMR spectrum, δ, ppm: 0.90 t (3H, CH_3), 1.04 t (3H, CH_3), 1.78 m (2H, CH_2), 2.06 m (2H, CH_2), 2.25 m (2H, CH_2), 3.58 s (1H, OH), 4.15 d (2H, CH_2O), 5.39 m (1H, CH=). Found, %: C 75.38; H 12.35. $C_8H_{16}O$. Calculated, %: C 75.00; H 12.50.

3-Methylpent-2-en-1-ol (IIIe). Yield 73%, bp 45–48°C (1–2 mm), n_D^{20} = 1.4511, purity 94%. IR spectrum, ν, cm^{-1}: 3335 (OH), 1662 (C=C). ^1H NMR spectrum, δ, ppm: 1.05 t (3H, CH_3), 2.01 s (3H, CH_3), 2.06 m (2H, CH_2), 3.39 s (1H, OH), 4.17 d (2H, CH_2O), 5.20 d.d (1H, CH=). Found, %: C 72.35; H 12.44. $C_6H_{12}O$. Calculated, %: C 72.00; H 12.00.

2-(Cyclopentylidene)ethanol (IIIh). Yield 76%, bp 66–67°C (1–2 mm), n_D^{20} = 1.4873, purity 96%. IR spectrum, ν, cm^{-1}: 3320 (OH), 1650 (C=C). ^1H NMR spectrum, δ, ppm: 1.47 m (4H, CH_2), 2.31 m (4H, CH_2), 3.31 s (1H, OH), 4.11 d (2H, CH_2O), 5.42 d.d (1H, CH=). Found, %: C 75.25; H 10.44. $C_7H_{12}O$. Calculated, %: C 75.00; H 10.71.

2-(Cyclohexylidene)ethanol (IIIg). Yield 78%, bp 80–84°C (1–2 mm), n_D^{20} = 1.4936, purity 90%. IR spectrum, ν, cm^{-1}: 3325 (OH), 1650 (C=C). ^1H NMR spectrum, δ, ppm: 1.48 m (2H, CH_2), 1.53 m (4H, CH_2), 2.17 m (2H, CH_2), 2.48 m (2H, CH_2), 3.40 s (1H, OH), 3.92 d (2H, CH_2O), 5.36 d.d (1H, CH=). Found, %: C 76.38; H 11.47. $C_8H_{14}O$. Calculated, %: C 76.19; H 11.11.

3-Methyl-4-phenylbut-2-en-1-ol (IIIh). Yield 93%, bp 104–106°C (1–2 mm), n_D^{20} = 1.5470, purity 87%. IR spectrum, ν, cm^{-1}: 3340 (OH), 1665 (C=C). ^1H NMR spectrum, δ, ppm: 1.55 s (3H, CH_3), 3.18 s (2H, CH_2), 4.12 d (2H, CH_2O), 4.31 s (1H, OH), 5.45 t (1H, CH=), 7.05 m (5H, C_6H_5). Found, %: C 81.22; H 8.49. $C_{11}H_{14}O$. Calculated, %: C 81.48; H 8.64.

3-Benzylpent-2-en-1-ol (IIIi). Yield 93%, bp 113–115°C (1–2 mm), n_D^{20} = 1.5270, purity 92%. IR spectrum, ν, cm^{-1}: 3341 (OH), 1662 (C=C). ^1H NMR spectrum, δ, ppm: 1.01 t (3H, CH_3), 2.12 m (2H, CH_2), 3.21 m (2H, CH_2), 3.96 d (2H, CH_2O), 4.20 s (1H, OH), 6.10 d.d (1H, CH=), 7.05 m (5H, C_6H_5). Found, %: C 81.47; H 9.36. $C_{12}H_{16}O$. Calculated, %: C 81.81; H 9.09.

3-Methyl-5-phenylpent-2-en-1-ol (IIIj). Yield 95%, bp 120–122°C (1–2 mm), n_D^{20} = 1.5344, purity 90%. IR spectrum, ν, cm^{-1}: 3340 (OH), 1665 (C=C). ^1H NMR spectrum, δ, ppm: 1.92 s (3H, CH_3), 2.03 m (2H, CH_2), 2.91 m (2H, CH_2), 4.50 s (1H, OH), 4.11 d (2H, CH_2O), 5.90 t (1H, CH=), 6.72 m (5H, C_6H_5). Found, %: C 81.57; H 8.56. $C_{10}H_{12}O$. Calculated, %: C 81.08; H 8.10.

3-Phenylbut-2-en-1-ol (IIIk). Yield 90%, bp 101–103°C (1–2 mm), n_D^{20} = 1.5267, purity 93%. IR spectrum, ν, cm^{-1}: 3342 (OH), 1664 (C=C). ^1H NMR spectrum, δ, ppm: 1.53 s (3H, CH_3), 3.98 s (2H, CH_2O), 4.10 s (1H, OH), 5.47 t (1H, CH=), 7.07 m (5H, C_6H_5). Found, %: C 81.58; H 9.39. $C_{12}H_{16}O$. Calculated, %: C 81.81; H 9.09.

Ethyl pent-4-enoates IVa–IVl (*general procedures***).** *a.* A mixture of 50 mmol of alkenol **IIIa–IIIk**, 60 mmol of triethyl orthoacetate, and 0.75 mmol of phenol was stirred for 9–10 h on heating at 135–140°C with simultaneous removal of ethanol liberated during the process. When ethanol was no longer distilled off (~0.05 mol), the mixture was heated for 3–5 h at 140–150°C, cooled, and dissolved in 100 ml of diethyl ether, and the solution was stirred, the formation of compounds **IV** being monitored by TLC. When the Claisen rearrangement was complete, the mixture was cooled to room temperature, treated with 1 N hydrochloric acid (2×50 ml) to decompose unreacted triethyl orthoacetate, and washed with a saturated solution of sodium hydrogen carbonate (2×50 ml) and water (2×50 ml). The ether layer was separated, dried over magnesium sulfate, and evaporated on a rotary evaporator under reduced pressure. The residue was subjected to either vacuum distillation or chromatographic separation in a column charged with silica gel. The concentration of the main substance in the product was determined by HPLC.

b. A mixture of 85 mmol of compound **IIIa–IIIk**, 170 mmol of triethyl orthoacetate, and 0.8 mmol of phosphoric acid was heated for 2 h at 120°C under stirring with simultaneous removal of ethanol liberated during the reaction. When ethanol was no longer distilled off, the temperature of the mixture was raised to 150°C, and the mixture was heated for 8 h at that temperature (TLC) and distilled under reduced pressure to isolate unreacted triethyl orthoacetate and ester **IVa–IVl**. The concentration of the main substance in the product was determined by HPLC.

Ethyl 3,3-diethylpent-4-enoate (IVa). Yield 70%, bp 78–80°C (1–2 mm), n_D^{20} = 1.4364, purity 94%. IR spectrum: ν 1645 cm^{-1} (C=C). ^1H NMR spectrum, δ, ppm: 0.69 t (6H, CH_3), 0.98 m (2H, CH_2), 1.11 t (3H, CH_3), 1.23 m (2H, CH_2), 2.08 s (2H, CH_2), 4.06 q (2H, CH_2O), 4.27 m (2H, $=CH_2$), 5.57 m (1H, CH=). Found, %: C 72.04; H 11.14. $C_{11}H_{20}O_2$. Calculated, %: C 71.73; H 10.86.

Ethyl 3-methyl-3-propylpent-4-enoate (IVb). Yield 63%, bp 78–81°C (1–2 mm), n_D^{20} = 1.4435, purity 92%. IR spectrum: ν 1644 cm^{-1} (C=C). ^1H NMR spectrum, δ, ppm: 0.81 t (3H, CH_3), 0.91 m (2H, CH_2), 1.06 s (3H, CH_3), 1.11 t (3H, CH_3), 1.21 m (1H, CH_2), 1.39 m (1H, CH_2), 2.09 d (1H, CH_2), 2.21 d (1H, CH_2), 4.13 q (2H, CH_2O), 4.62 m (2H, $=CH_2$), 5.48 m (1H, CH=). Found, %: C 72.12; H 11.07. $C_{11}H_{20}O_2$. Calculated, %: C 71.73; H 10.86.

Ethyl 3,3-dipropylpent-4-enoate (IVc). Yield 77%, bp 63–65°C (4–5 mm), n_D^{20} = 1.4312, purity 94%. IR spectrum: ν 1642 cm^{-1} (C=C). ^1H NMR spectrum, δ, ppm: 0.77 d.t (6H, CH_3), 0.83 m (4H, CH_2), 1.25 t (3H, CH_3), 1.26 m (2H, CH_2), 1.46 m (2H, CH_2), 2.21 s (2H, CH_2), 4.15 q (2H, CH_2O), 4.77 m (2H, $=CH_2$), 5.63 m (1H, CH=). Found, %: C 73.94; H 11.46. $C_{13}H_{24}O_2$. Calculated, %: C 73.58; H 11.32.

Ethyl 3-ethyl-3-propylpent-4-enoate (IVd). Yield 59%, bp 82–84°C (1–2 mm), n_D^{20} = 1.4410, purity 95%. IR spectrum: ν 1645 cm^{-1} (C=C). ^1H NMR spectrum, δ, ppm: 0.78 m (6H, CH_3), 0.86 m (2H, CH_2), 1.11 m (2H, CH_2), 1.21 t (3H, CH_3), 1.46 m (2H, CH_2), 2.11 d (1H, CH_2), 2.19 d (1H, CH_2), 4.13 q (2H, CH_2O), 5.02 m (2H, $=CH_2$), 5.72 m (1H, CH=). Found, %: C 72.99; H 11.53. $C_{12}H_{22}O_2$. Calculated, %: C 72.72; H 11.11.

Ethyl 3-ethyl-3-methylpent-4-enoate (IVe). Yield 60%, bp 82–84°C (1–2 mm), n_D^{20} = 1.4410, purity 95%.

IR spectrum: ν 1644 cm^{-1} (C=C). ^1H NMR spectrum, δ, ppm: 0.77 t (3H, CH_3), 1.06 s (3H, CH_3), 1.14 m (1H, CH_2), 1.23 t (3H, CH_3), 1.33 m (1H, CH_2), 2.15 d (1H, CH_2), 2.23 d (1H, CH_2), 4.09 q (2H, CH_2O), 5.08 m (2H, $=CH_2$), 5.86 m (1H, CH=). Found, %: C 70.27; H 10.35. $C_{10}H_{18}O_2$. Calculated, %: C 70.58; H 10.58.

Ethyl (1-vinylcyclopentyl)acetate (IVf). Yield 72%, bp 87–90°C (1–2 mm), n_D^{20} = 1.4292, purity 92%. IR spectrum: ν 1645 cm^{-1} (C=C). ^1H NMR spectrum, δ, ppm: 1.09 t (3H, CH_3), 1.62 m (2H, CH_2), 1.67 m (2H, CH_2), 1.69 m (2H, CH_2), 1.91 m (2H, CH_2), 2.12 s (2H, CH_2), 3.87 q (2H, CH_2O), 4.99 d.d (2H, $=CH_2$), 5.63 t (1H, CH=). Found, %: C 72.38; H 9.55. $C_{11}H_{18}O_2$. Calculated, %: C 72.52; H 9.89.

Ethyl (1-vinylcyclohexyl)acetate (IVg). Yield 76%, bp 66–69°C (1–2 mm), n_D^{20} = 1.4525, purity 87%. IR spectrum: ν 1645 cm^{-1} (C=C). ^1H NMR spectrum, δ, ppm: 1.11 t (3H, CH_3), 1.41 m (6H, CH_2), 1.45 m (2H, CH_2), 1.50 m (2H, CH_2), 3.95 q (2H, CH_2O), 5.01 m (2H, $=CH_2$), 5.63 d.d (1H, CH=). Found, %: C 73.27; H 9.86. $C_{12}H_{20}O_2$. Calculated, %: C 73.46; H 10.20.

Ethyl 3-benzyl-3-methylpent-4-enoate (IVh). Yield 85%, bp 104–106°C (1–2 mm), n_D^{20} = 1.4956, purity 95%. IR spectrum: ν 1639 cm^{-1} (C=C). ^1H NMR spectrum, δ, ppm: 1.11 t (3H, CH_3), 1.19 s (3H, CH_3), 2.16 d (1H, CH_2), 2.36 d (1H, CH_2), 2.47 d (1H, CH_2), 2.87 d (1H, CH_2), 4.04 q (2H, CH_2O), 5.00 m (2H, $=CH_2$), 5.69 m (1H, CH=), 7.08 m (5H, C_6H_5). Found, %: C 77.72; H 8.91. $C_{15}H_{20}O_2$. Calculated, %: C 77.58; H 8.62.

Ethyl 3-benzyl-3-ethylpent-4-enoate (IVi). Yield 82%, bp 90–93°C (1–2 mm), n_D^{20} = 1.4950, purity 93%. IR spectrum: ν 1640 cm^{-1} (C=C). ^1H NMR spectrum, δ, ppm: 0.82 t (3H, CH_3), 1.06 m (2H, CH_2), 1.11 t (3H, CH_3), 2.0 m (1H, CH_2), 2.02 d (1H, CH_2), 2.56 d (1H, CH_2), 2.80 d (1H, CH_2), 4.08 q (2H, CH_2), 4.97 m (2H, CH_2=), 5.71 m (1H, =CH), 6.98 d (2H, C_6H_5), 7.15 m (3H, C_6H_5). Found, %: C 78.34; H 9.25. $C_{16}H_{22}O_2$. Calculated, %: C 78.04; H 8.94.

Ethyl 3-methyl-3-(2-phenylethyl)pent-4-enoate (IVj). Yield 78%, bp 125–127°C (1–2 mm), n_D^{20} = 1.4943, purity 95%. IR spectrum: ν 1640 cm^{-1} (C=C). ^1H NMR spectrum, δ, ppm: 1.25 s (3H, CH_3), 1.30 t (3H, CH_3), 1.63 m (1H, CH_2), 1.83 m (1H, CH_2), 2.12 d (1H, CH_2), 2.38 d (1H, CH_2), 2.61 m (2H, CH_2CH_2), 4.15 q (2H, CH_2O), 5.10 m (2H, $=CH_2$), 5.96 m (1H, CH=), 7.35 m (5H, C_6H_5). Found, %: C 78.43; H 9.37. $C_{16}H_{22}O_2$. Calculated, %: C 78.04; H 8.94.

Ethyl 3-methyl-3-phenylpent-4-enoate (IVk). Yield 60%, bp 71–73°C (1–2 mm), n_D^{20} = 1.4626, purity 89%. IR spectrum: ν 1641 cm^{-1} (C=C). ^1H NMR spectrum, δ, ppm: 1.07 t (3H, CH_3), 1.48 s (3H, CH_3), 2.12 d (1H, CH_2), 2.32 d (1H, CH_2), 3.91 q (2H, CH_2O), 5.05 m (2H, $=CH_2$), 6.02 d.d (1H, CH=), 7.28 m (5H, C_6H_5). Found, %: C 77.54; H 8.59. $C_{14}H_{18}O_2$. Calculated, %: C 77.06; H 8.25.

Ethyl 3-phenylpent-4-enoate (IVl). Yield 52%, bp 102–104°C (1–2 mm), n_D^{20} = 1.4853, purity 93%. IR spectrum: ν 1639 cm^{-1} (C=C). ^1H NMR spectrum, δ, ppm: 1.21 t (3H, CH_3), 2.51 m (1H, CH_2), 2.71 m (1H, CH_2), 3.67 m (1H, CH), 3.97 q (2H, CH_2O), 4.97 m (2H, $=CH_2$), 5.95 m (1H, CH=), 7.3 m (5H, C_6H_5). Found, %: C 77.25; H 8.24. $C_{13}H_{16}O_2$. Calculated, %: C 76.47; H 7.84.

Ethyl 4-bromo-6,6,6-trichlorohexanoates Va–Vl (*general procedure*). A mixture of 130 mmol of bromotrichloromethane, 43 mmol of ethyl pentenoate **IVa–IVl**, 45 mmol of 2-aminoethanol, 1 mmol of copper(I) chloride, and 310 mmol of *tert*-butyl alcohol was heated to the boiling point (84–85°C) and was maintained boiling under stirring for 6 h. The progress of the reaction was monitored by GLC (sample were withdrawn from the mixture in 2 h and then every 1 h until the reaction was complete). Excess *tert*-butyl alcohol and bromotrichloromethane were removed under reduced pressure on a rotary evaporator, and the residue was purified by preparative column chromatography on silica gel. The purity of the products was determined by HPLC.

Ethyl 4-bromo-6,6,6-trichloro-3,3-diethylhexanoate (Va). Yield 73% (51% after chromatographic purification), purity 98%. ^1H NMR spectrum, δ, ppm: 0.83 t (6H, CH_3), 1.23 t (3H, CH_3), 1.28 m (2H, CH_2), 1.53 m (2H, CH_2), 2.37 s (2H, CH_2), 3.26 m and 3.36 m (1H each, 5-H), 4.07 q (2H, CH_2O), 4.21 d (1H, CHBr). Found, %: C 37.41; H 4.94; Br 21.03; Cl 27.98. $C_{12}H_{20}BrCl_3O_2$. Calculated, %: C 37.68; H 5.27; Br 20.89; Cl 27.80.

Ethyl 4-bromo-6,6,6-trichloro-3-methyl-3-propylhexanoate (Vb). Yield 78% (62% after chromatographic purification), purity 97%. ^1H NMR spectrum, δ, ppm: 0.86 t (3H, CH_3), 1.14 s (3H, CH_3), 1.24 t (3H, CH_3), 1.32 m (2H, CH_2), 1.44 m (1H, CH_2), 1.54 m (1H, CH_2), 2.44 d (1H, CH_2), 2.58 d (1H, CH_2), 3.04 d.d and 3.19 d (1H each, 5-H), 4.12 q (2H, CH_2O), 4.35 m (1H, CHBr). Found, %: C 37.34;

H 5.11; Br 21.17; Cl 28.10. $C_{12}H_{20}BrCl_3O_2$. Calculated, %: C 37.68; H 5.27; Br 20.89; Cl 27.80.

Ethyl 4-bromo-6,6,6-trichloro-3,3-dipropylhexanoate (Vc). Yield 69% (49% after chromatographic purification), purity 98%. ^{1}H NMR spectrum, δ, ppm: 0.75 t (6H, CH_3), 1.02 t (3H, CH_3), 1.10 m (2H, CH_2), 1.15 m (2H, CH_2), 1.25 m (2H, CH_2), 1.38 m (2H, CH_2), 2.26 s (2H, CH_2), 3.12 d.d and 3.25 d (1H each, 5-H), 3.92 q (2H, CH_2O), 4.28 d (1H, CHBr). Found, %: C 40.75; H 5.68; Br 19.74; Cl 26.07. $C_{14}H_{24}BrCl_3O_2$. Calculated, %: C 40.92; H 5.84; Br 19.48; Cl 25.94.

Ethyl 4-bromo-6,6,6-trichloro-3-ethyl-3-propylhexanoate (Vd). Yield 73% (58% after chromatographic purification), purity 98%. ^{1}H NMR spectrum, δ, ppm: 0.90 t (6H, CH_3), 1.21 m (1H, CH_2), 1.26 t (3H, CH_3), 1.30 m (1H, CH_2), 1.48 m (1H, CH_2), 1.52 m (1H, CH_2), 2.38 d (1H, CH_2), 2.51 d (1H, CH_2), 3.16 d and 3.29 m (1H each, 5-H), 4.02 q (2H, CH_2O), 4.57 m (1H, CHBr). Found, %: C 40.54; H 5.62; Br 19.63; Cl 26.21. $C_{12}H_{22}BrCl_3O_2$. Calculated, %: C 39.34; H 5.54; Br 20.17; Cl 26.86.

Ethyl 4-bromo-6,6,6-trichloro-3-ethyl-3-methylhexanoate (Ve). Yield 81% (57% after chromatographic purification), purity 96%. ^{1}H NMR spectrum, δ, ppm: 0.95 t (3H, CH_3), 1.13 s (3H, CH_3), 1.26 t (3H, CH_3), 1.37 m (1H, CH_2), 1.61 m (1H, CH_2), 2.37 d (1H, CH_2), 2.48 d (1H, CH_2), 3.19 d and 3.32 m (1H each, 5-H), 4.07 q (2H, CH_2O), 4.48 m (1H, CHBr). Found, %: C 35.64; H 4.71; Br 21.98; Cl 29.12. $C_{11}H_{18}BrCl_3O_2$. Calculated, %: C 35.82; H 4.88; Br 21.70; Cl 28.90.

Ethyl 2-[1-(1-bromo-2,2,2-trichloroethyl)cyclopentyl]acetate (Vf). Yield 77% (55% after chromatographic purification), purity 98%. ^{1}H NMR spectrum, δ, ppm: 1.27 t (3H, CH_3), 1.46 m (2H, CH_2), 1.55 m (2H, CH_2), 1.68 m (4H, CH_2), 2.47 s (2H, CH_2), 3.26 d and 3.39 d.d (1H each, 5-H), 4.08 q (2H, CH_2O), 4.51 m (1H, CHBr). Found, %: C 37.52; H 4.51; Br 21.22; Cl 28.31. $C_{12}H_{18}BrCl_3O_2$. Calculated, %: C 37.84; H 4.73; Br 21.02; Cl 27.98.

Ethyl 2-[1-(1-bromo-2,2,2-trichloroethyl)cyclohexyl]acetate (Vg). Yield 78% (64% after chromatographic purification), purity 97%. ^{1}H NMR spectrum, δ, ppm: 1.07 t (3H, CH_3), 1.49 m (6H, CH_2), 1.58 m (2H, CH_2), 1.65 m (2H, CH_2), 2.43 s (2H, CH_2), 3.13 m and 3.26 m (1H each, 5-H), 3.85 q (2H, CH_2O), 4.58 m (1H, CHBr). Found, %: C 39.41; H 4.87; Br 20.43; Cl 27.21. $C_{13}H_{20}BrCl_3O_2$. Calculated, %: C 39.54; H 5.06; Br 20.27; Cl 26.99.

Ethyl 3-benzyl-4-bromo-6,6,6-trichloro-3-methylhexanoate (Vh). Yield 75% (52% after chromatographic purification), purity 98%. ^{1}H NMR spectrum, δ, ppm: 1.21 t (3H, CH_3), 1.32 s (3H, CH_3), 2.49 d (1H, CH_2), 2.64 d (1H, CH_2), 2.79 d (1H, CH_2), 2.98 d (1H, CH_2), 3.09 d and 3.25 m (1H each, 5-H), 4.01 q (2H, CH_2O), 4.27 m (1H, CHBr), 7.18 m (5H, C_6H_5). Found, %: C 44.37; H 4.31; Br 18.72; Cl 24.95. $C_{16}H_{20}BrCl_3O_2$. Calculated, %: C 44.59; H 4.64; Br 18.58; Cl 24.73.

Ethyl 3-benzyl-4-bromo-6,6,6-trichloro-3-ethylhexanoate (Vi). Yield 63% (47% after chromatographic purification), purity 97%. ^{1}H NMR spectrum, δ, ppm: 0.95 t (3H, CH_3), 1.18 t (3H, CH_3), 1.26 m (1H, CH_2), 1.43 m (1H, CH_2), 2.17 m (2H, CH_2), 2.68 m (2H, CH_2), 3.15 d and 3.65 d.d (1H each, 5-H), 4.10 q (2H, CH_2O), 4.68 m (1H, CHBr), 7.42 m (5H, C_6H_5). Found, %: C 45.62; H 5.07; Br 18.23; Cl 24.16. $C_{17}H_{22}BrCl_3O_2$. Calculated, %: C 45.89; H 4.94; Br 17.99; Cl 23.95.

Ethyl 4-bromo-6,6,6-trichloro-3-methyl-3-(2-phenylethyl)hexanoate (Vj). Yield 68% (48% after chromatographic purification), purity 96%. ^{1}H NMR spectrum, δ, ppm: 1.19 m (6H, CH_3), 1.54 m (1H, CH_2), 1.81 m (1H, CH_2), 2.38 d (1H, CH_2), 2.51 d (1H, CH_2), 2.59 d.d (2H, CH_2), 3.09 d and 3.22 m (1H each, 5-H), 4.05 m (2H, CH_2O), 4.53 m (1H, CHBr), 7.12 m (5H, C_6H_5). Found, %: C 45.57; H 5.12; Br 18.14; Cl 24.22. $C_{17}H_{22}BrCl_3O_2$. Calculated, %: C 45.89; H 4.94; Br 17.99; Cl 23.95.

Ethyl 4-bromo-6,6,6-trichloro-3-methyl-3-phenylhexanoate (Vk). Yield 65% (49% after chromatographic purification), purity 93%. ^{1}H NMR spectrum, δ, ppm: 0.97 t (3H, CH_3), 1.68 s (3H, CH_3), 2.63 d (1H, CH_2), 2.78 d (1H, CH_2), 3.18 d and 3.31 m (1H each, 5-H), 4.16 q (2H, CH_2O), 4.75 m (1H, CHBr), 7.29 m (5H, C_6H_5). Found, %: C 43.13; H 4.12; Br 19.39; Cl 25.73. $C_{15}H_{18}BrCl_3O_2$. Calculated, %: C 43.21; H 4.32; Br 19.20; Cl 25.57.

Ethyl 4-bromo-6,6,6-trichloro-3-phenylhexanoate (Vl). Yield 73% (52% after chromatographic purification), purity 94%. ^{1}H NMR spectrum, δ, ppm: 1.12 t (3H, CH_3), 2.72 m (2H, CH_2), 3.15 m and 3.32 m (1H each, 5-H), 3.72 m (1H, CH), 4.04 m (2H, CH_2O), 4.82 m (1H, CHBr), 7.38 m (5H, C_6H_5). Found, %: C 41.54; H 3.76; Br 20.06; Cl 26.64. $C_{14}H_{16}BrCl_3O_2$. Calculated, %: C 41.73; H 3.97; Br 19.87; Cl 26.45.

Ethyl cyclopropanecarboxylates VIa–VIk (*general procedure*). A solution of 110 mmol of sodium

ethoxide prepared from 2.53 g of metallic sodium and 100 ml of anhydrous ethanol was added to a solution of 50 mmol of ester **Va–Vl** in 200 ml of anhydrous ethanol, cooled to 0°C. The mixture was slowly (over a period of 1 h) allowed to warm up to room temperature under stirring and was then heated for 1 h under reflux (the solution turned colorless, and a solid separated). The mixture was evaporated to a volume of 30 ml, 100 g of ice was added, and the mixture was neutralized with ice-cold 1 N hydrochloric acid and extracted with diethyl ether (2×100 ml). The ether extract was washed with a saturated solution of sodium hydrogen carbonate (2×50 ml) and a solution of sodium chloride (2×50 ml) and dried over sodium sulfate. The solvent was distilled off under reduced pressure on a rotary evaporator, and the residue was subjected to column chromatography on silica gel. The products were light yellow oily substances (yield 45–55% after chromatographic purification). Their purity was determined by HPLC.

Ethyl 3-(2,2-dichlorovinyl)-2,2-diethylcyclopropane-1-carboxylate (VIa). Yield 73% (47% after chromatographic purification), purity 96%. IR spectrum: ν 1619 cm^{-1} (C=C). ^{1}H NMR spectrum, δ, ppm: *cis* isomer: 0.71 t (3H, CH_3), 0.79 t (3H, CH_3), 1.10 t (3H, CH_3), 1.12 m (1H, CH_2), 1.40 m (1H, CH_2), 1.54 m (2H, CH_2), 1.64 d (1H, 1-H), 1.86 t (1H, 3-H), 3.97 q (2H, OCH_2), 6.24 d (1H, CH=); *trans* isomer: 0.68 t (3H, CH_3), 0.76 t (3H, CH_3), 1.07 t (3H, CH_3), 1.14 m (1H, CH_2), 1.35 m (1H, CH_2), 1.37 m (1H, CH_2), 1.43 d (1H, 1-H), 1.52 m (1H, CH_2), 2.03 d.d (1H, 3-H), 3.95 q (2H, OCH_2), 5.45 d (1H, CH=). ^{13}C NMR spectrum, δ_C, ppm: *cis* isomer: 10.2, 10.3, 10.4, 17.1, 30.5, 31.3, 31.9, 37.4, 60.3, 120.2, 124.8, 170.5; *trans* isomer: 10.3, 10.5, 14.2, 21.6, 25.1, 32.5, 34.5, 39.0, 60.5, 121.4, 127.1, 170.9. Mass spectrum: *m*/*z* 265 $[M]^+$. Found, %: C 54.44; H 7.17; Cl 27.84. $C_{12}H_{18}Cl_2O_2$. Calculated, %: C 54.33; H 6.79; Cl 26.79. *M* 265.21.

Ethyl 3-(2,2-dichlorovinyl)-2-methyl-2-propylcyclopropane-1-carboxylate (VIb). Yield 64% (49% after chromatographic purification), purity 94%. IR spectrum: ν 1619 cm^{-1} (C=C). ^{1}H NMR spectrum, δ, ppm: *c*-Me-*t*-Pr-*c*-$CHCCl_2$: 0.80 t (3H, CH_3), 1.09 s (3H, CH_3), 1.14 t (3H, CH_3), 1.34 m (2H, CH_2), 1.40 m (1H, CH_2), 1.42 m (1H, CH_2), 1.70 d (1H, 1-H), 1.89 t (1H, 3-H), 4.09 q (2H, OCH_2), 6.19 d (1H, CH=); *t*-Me-*c*-Pr-*c*-$CHCCl_2$: 0.85 t (3H, CH_3), 1.07 s (3H, CH_3), 1.18 t (3H, CH_3), 1.25 m (1H, CH_2), 1.28 m (1H, CH_2), 1.36 m (2H, CH_2), 1.73 d (1H, 1-H), 1.92 t (1H, 3-H), 4.03 q (2H, OCH_2), 6.24 d (1H, CH=); *c*-Me-*t*-Pr-*t*-$CHCCl_2$: 0.89 t (3H, CH_3), 1.10 s (3H, CH_3), 1 22 t (3H, OCH_2CH_3), 1.35 m (2H, CH_2), 1.47 m (1H, CH_2), 1.48 d (1H, 1-H), 1.49 m (1H, CH_2), 2.06 t (1H, 3-H), 3.99 q (2H, OCH_2), 5.49 d (1H, CH=); *t*-Me-*t*-Pr-*c*-$CHCCl_2$: 0.92 t (3H, CH_3), 1.02 s (3H, CH_3), 1.15 t (3H, CH_3), 1.17 m (1H, CH_2), 1.22 m (1H, CH_2), 1.30 m (2H, CH_2), 1.48 d (1H, 1-H), 2.10 t (1H, 3-H), 4.02 q (2H, OCH_2), 5.47 d (1H, CH=). ^{13}C NMR spectrum, δ_C, ppm: *c*-Me-*t*-Pr-*c*-$CHCCl_2$: 12.2, 13.6, 14.3, 19.7, 28.7, 31.3, 31.8, 44.4, 60.3, 120.3, 125.0, 170.8; *t*-Me-*c*-Pr-*c*-$CHCCl_2$: 13.9, 14.4, 19.7, 25.7, 28.5, 29.9, 30.2, 31.8, 60.1, 120.4, 125.0, 170.0; *c*-Me-*t*-Pr-*t*-$CHCCl_2$: 14.0, 14.3, 17.1, 19.6, 32.7, 32.9, 34.8, 35.4, 60.6, 121.7, 127.1, 170.9; *t*-Me-*t*-Pr-*c*-$CHCCl_2$: 13.6, 14.2, 19.8, 19.8, 32.4, 32.7, 34.6, 38.7, 60.4, 121.8, 128.3, 171.2. Mass spectrum, *m*/*z*: 263 $[M]^+$. Found, %: C 54.51; H 7.08; Cl 27.77. $C_{12}H_{18}Cl_2O_2$. Calculated, %: C 54.33; H 6.79; Cl 26.79. *M* 263.20.

Ethyl 3-(2,2-dichlorovinyl)-2,2-dipropylcyclopropane-1-carboxylate (VIc). Yield 63% (52% after chromatographic purification), purity 95%. IR spectrum: ν 1619 cm^{-1} (C=C). ^{1}H NMR spectrum, δ, ppm: *cis* isomer: 0.72 t (3H, CH_3), 0.75 t (3H, CH_3), 1.02 m (1H, CH_2), 1.07 t (3H, CH_3), 1.25 m (1H, CH_2), 1.27 m (2H, CH_2), 1.37 m (1H, CH_2), 1.42 m (1H, CH_2), 1.48 t (2H, CH_2), 1.62 d (1H, 1-H), 1.84 t (1H, 3-H), 3.95 q (2H, OCH_2), 6.23 d (1H, CH=); *trans* isomer: 0.70 t (3H, CH_3), 0.73 t (3H, CH_3), 1.14 m (3H, CH_3), 1.16 m (1H, CH_2), 1.19 m (1H, CH_2), 1.21 m (1H, CH_2), 1.24 m (1H, CH_2), 1.28 m (1H, CH_2), 1.35 m (1H, CH_2), 1.39 m (1H, CH_2), 1.43 d (1H, 1-H), 2.03 d.d (1H, 3-H), 3.95 q (2H, OCH_2), 5.44 d (1H, CH=). ^{13}C NMR spectrum, δ, ppm: *cis* isomer: 14.0, 14.1, 14.2, 19.2, 19.3, 27.0, 31.1, 32.0, 35.1, 40.5, 60.2, 120.1, 124.9, 170.5; *trans* isomer: 13.9, 14.0, 14.2, 19.3, 19.5, 31.3, 32.2, 34.5, 34.9, 36.72, 60.5, 121.3, 127.1, 170.8. Mass spectrum: *m*/*z* 293 $[M]^+$. Found, %: C 57.62; H 7.32; Cl 24.67. $C_{14}H_{22}Cl_2O_2$. Calculated, %: C 57.33; H 7.50; Cl 24.23. *M* 293.26.

Ethyl 3-(2,2-dichlorovinyl)-2-ethyl-2-propylcyclopropane-1-carboxylate (VId). Yield 63% (54% after chromatographic purification), purity 94%. IR spectrum: ν 1619 cm^{-1} (C=C). ^{1}H NMR spectrum, δ, ppm: *c*-Et-*t*-Pr-*c*-$CHCCl_2$: 0.80 t (3H, CH_3), 0 82 t (3H, CH_3), 1.14 t (3H, CH_3), 1.26 m (2H, CH_2), 1.28 m (2H, CH_2), 1.39 m (2H, SH_2), 1.73 d (1H, 1-H), 1.99 t (1H, 3-H), 4.01 q (2H, OCH_2), 6.18 d (1H, CH=). ^{13}C NMR spectrum, δ_C, ppm: 10.8, 13.9, 14.1, 19.4, 29.9, 31.6, 31.9, 34.9, 43.8, 60.1, 121.2, 124.8, 172.1.

Mass spectrum: *m*/*z* 279 $[M]^+$. Found, %: C 56.21; H 7.38; Cl 25.77. $C_{13}H_{20}Cl_2O_2$. Calculated, %: C 55.91; H 7.16; Cl 25.44. *M* 279.23.

Ethyl 3-(2,2-dichlorovinyl)-2-ethyl-2-methylcyclopropane-1-carboxylate (VIe). Yield 70% (52% after chromatographic purification), purity 96%. IR spectrum: ν 1619 cm^{-1} (C=C). ^1H NMR spectrum, δ, ppm: *c*-Me-*t*-Et-*c*-$CHCCl_2$: 0.82 t (3H, CH_3), 1.04 s (3H, CH_3), 1.12 t (3H, CH_3), 1.24 m (2H, CH_2), 1.65 d (1H, 1-H), 1.87 t (1H, 3-H), 4.09 q (2H, OCH_2), 6.20 d (1H, CH=); *t*-Me-*c*-Et-*c*-$CHCCl_2$: 0.82 t (3H, CH_3), 1.04 s (3H, CH_3), 1.18 t (3H, CH_3), 1.73 d (1H, 1-H), 1.92 t (1H, 3-H), 4.03 q (2H, OCH_2), 6.24 d (1H, CH=); *c*-Me-*t*-Et-*t*-$CHCCl_2$: 0.80 t (3H, CH_3), 1.05 s (3H, CH_3), 1.07 t (3H, CH_3), 1.17 m (1H, CH_2), 1.28 m (1H, CH_2), 1.42 d (1H, 1-H), 2.04 m (1H, 3-H), 3.95 q (2H, OCH_2), 5.44 d (1H, CH=). ^{13}C NMR spectrum, δ_C, ppm: *c*-Me-*t*-Et-*c*-$CHCCl_2$: 10.4, 11.7, 14.3, 30.6, 32.2, 32.9, 35.5, 60.3, 120.3, 124.9, 171.2; *t*-Me-*c*-Et-*c*-$CHCCl_2$: 10.5, 14.2, 24.9, 31.1, 31.6, 32.4, 35.1, 60.2, 120.2, 125.0, 170.4; *c*-Me-*t*-Et-*t*-$CHCCl_2$: 10.6, 14.3, 16.4, 29.5, 32.9, 33.6, 34.4, 60.5, 121.5, 127.09, 170.8. Mass spectrum: *m*/*z* 251 $[M]^+$. Found, %: C 52.90; H 6.64; Cl 28.56. $C_{11}H_{16}Cl_2O_2$. Calculated, %: C 52.58; H 6.37; Cl 28.28. *M* 251.17.

Ethyl 2-(2,2-dichlorovinyl)spiro[2.4]heptane-1-carboxylate (VIf). Yield 58% (44% after chromatographic purification), purity 95%. IR spectrum: ν 1615 cm^{-1} (C=C). ^1H NMR spectrum, δ, ppm: 1.27 t (3H, CH_3), 1.56 d (1H, 1-H), 1.69 m (4H, CH_2), 1.73 d (2H, CH_2), 1.79 t (2H, CH_2), 2.38 d.d (1H, 2-H), 4.15 q (2H, OCH_2), 5.52 d (1H, CH=). ^{13}C NMR spectrum, δ_C, ppm: 14.3, 25.5, 26.2, 29.9, 32.1, 33.1, 34.1, 36.2, 60.4, 121.4, 126.9, 170.3. Mass spectrum: *m*/*z* 263 $[M]^+$. Found, %: C 54.46; H 5.82; Cl 27.38. $C_{12}H_{16}Cl_2O_2$. Calculated, %: C 54.75; H 6.08; Cl 26.99. *M* 263.13.

Ethyl 2-(2,2-dichlorovinyl)spiro[2.5]octane-1-carboxylate (VIg). Yield 57% (44% after chromatographic purification), purity 96%. IR spectrum: ν 1615 cm^{-1} (C=C). ^1H NMR spectrum, δ, ppm: 1.07 t (3H, CH_3), 1.36 m (2H, 6-H), 1.47 m (1H, 4-H or 8-H), 1.48 m (2H, 5-H or 7-H), 1.53 m (2H, 5-H or 7-H), 1,59 m (1H, 8-H or 4-H), 1.61 m (1H, 4-H or 8-H), 1.63 m (1H, 8-H or 4-H), 1.69 m (1H, 1-H), 2.24 d.d (1H, 2-H), 4.11 q (2H, OCH_2), 5.59 d (1H, CH=). ^{13}C NMR spectrum, δ_C, ppm: 14.32, 25.4, 25.5, 26.0, 29.9, 32.5, 32.6, 33.0, 36.9, 60.4, 121.9, 126.5, 170.4. Mass spectrum: *m*/*z* 277 $[M]^+$. Found, %: C 56.08; H 6.15; Cl 24.67. $C_{13}H_{18}Cl_2O_2$. Calculated, %: C 56.31; H 6.49; Cl 25.63. *M* 277.21.

Ethyl 2-benzyl-3-(2,2-dichlorovinyl)-2-methylcyclopropane-1-carboxylate (VIh). Yield 63% (51% after chromatographic purification), purity 96%. IR spectrum: ν 1620 cm^{-1} (C=C). ^1H NMR spectrum, δ, ppm: *c*-Me-*t*-Bzl-*c*-$CHCCl_2$: 1.13 s (3H, CH_3), 1.18 t (3H, CH_3), 1.93 d (1H, 1-H), 2.15 t (1H, 3-H), 2.61 d (1H, C**H**$_2$Ph), 2.71 d (1H, C**H**$_2$Ph), 4.05 q (2H, OCH_2), 6.29 d (1H, CH=), 7.10–7.24 m (5H, Ph); *t*-Me-*c*-Bzl-*c*-$CHCCl_2$: 1.04 s (3H, CH_3), 1.15 t (3H, CH_3), 1.89 d (1H, 1-H), 2.08 t (1H, 3-H), 2.9 d (1H, C**H**$_2$Ph), 3.08 d (1H, C**H**$_2$Ph), 4.05 q (2H, OCH_2), 6.49 d (1H, CH=), 7.09–7.23 m (5H, Ph); *c*-Me-*t*-Bzl-*t*-$CHCCl_2$: 1.08 s (3H, CH_3), 1.18 t (3H, CH_3), 1.85 d (1H, 1-H), 2.27 t (1H, 3-H), 2.60 d (1H, C**H**$_2$Ph), 2.67 d (1H, C**H**$_2$Ph), 4.07 q (2H, OCH_2), 5.69 d (1H, CH=), 7.12–7.26 m (5H, Ph); *t*-Me-*c*-Bzl-*t*-$CHCCl_2$: 1.00 s (3H, CH_3), 1.18 t (3H, CH_3), 1.66 d (1H, 1-H), 2.48 t (1H, 3-H), 2.84 d (1H, C**H**$_2$Ph), 2.95 d (1H, C**H**$_2$Ph), 4.07 q (2H, OCH_2), 5.53 d (1H, CH=), 7.12–7.26 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: *c*-Me-*t*-Bzl-*c*-$CHCCl_2$: 13.0, 14.2, 30.2, 30.7, 31.6, 47.1, 60.6, 120.8, 124.8, 126.7–137.8, 170.9; *t*-Me-*c*-Bzl-*c*-$CHCCl_2$: 14.4, 25.7, 29.1, 31.8, 32.8, 34.0, 60.4, 121.0, 124.9, 126.5–137.9, 171.0; *c*-Me-*t*-Bzl-*t*-$CHCCl_2$: 14.4, 17.4, 32.2, 32.8, 34.5, 42.0, 60.9, 122.2, 126.5–138.5, 126.6, 171.2; *t*-Me-*c*-Bzl-*t*-$CHCCl_2$: 14.5, 19.9, 32.4, 33.4, 34.7, 38.9, 60.7, 122.3, 126.5–138.5, 126.9, 171.1. Mass spectrum: *m*/*z* 313 $[M]^+$. Found, %: C 61.55; H 6.09; Cl 22.99. $C_{16}H_{18}Cl_2O_2$. Calculated, %: C 61.34; H 5.75; Cl 22.68. *M* 313.24.

Ethyl 2-benzyl-3-(2,2-dichlorovinyl)-2-ethylcyclopropane-1-carboxylate (VIi). Yield 59% (45% after chromatographic purification), purity 95%. IR spectrum: ν 1620 cm^{-1} (C=C). ^1H NMR spectrum, δ, ppm: *c*-Et-*t*-Bzl-*c*-$CHCCl_2$: 0.85 t (3H, CH_3), 1.18 t (3H, CH_3), 1.44 m (1H, CH_2), 1.50 m (1H, CH_2), 1.83 d (1H, 1-H), 2.12 t (1H, 3-H), 2.60 d (1H, C**H**$_2$Ph), 2.77 d (1H, C**H**$_2$Ph), 4.02 q (2H, OCH_2), 6.33 d (1H, CH=), 7.09–7.25 m (5H, Ph); *c*-Bzl-*t*-Et-*c*-$CHCCl_2$: 0.83 t (3H, CH_3), 1.07 m (1H, CH_2), 1.18 t (3H, CH_3), 1.38 m (1H, CH_2), 1.85 d (1H, 1-H), 2.06 t (1H, 3-H), 2.92 d (1H, C**H**$_2$Ph), 3.05 d (1H, C**H**$_2$Ph), 4.05 q (2H, OCH_2), 6.45 d (1H, CH=), 7.02–7.20 m (5H, Ph); *c*-Et-*t*-Bzl-*t*-$CHCCl_2$: 0.82 t (3H, CH_3), 1.14 t (3H, CH_3), 1.35 m and 1.42 m (1H each, CH_2), 1.80 d (1H, 1-H), 2.25 t (1H, 3-H), 2.66 m (1H, C**H**$_2$Ph), 2.68 m (1H, C**H**$_2$Ph), 4.08 q (2H, OCH_2), 5.65 d (1H, CH=), 7.09–7.23 m (5H, Ph); *c*-Bzl-*t*-Et-*t*-$CHCCl_2$: 0.83 t (3H, CH_3), 1.18 t (3H, CH_3), 1.20 m (1H, CH_2), 1.25 m (1H, CH_2), 1.68 d (1H, 1-H),

2.49 m (1H, 3-H), 2.90 d (1H, C**H**$_2$Ph), 2.98 d (1H, C**H**$_2$Ph), 4.07 q (2H, OCH_2), 5.57 d (1H, CH=), 7.10–7.26 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: *c*-Et-*t*-Bzl-*c*-$CHCCl_2$: 10.3, 14.3, 18.5, 29.7, 31.0, 36.6, 42.6, 60.5, 120.5, 120.6–138.9, 124.6, 170.5; *c*-Bzl-*t*-Et-*c*-$CHCCl_2$: 10.4, 14.3, 30.3, 31.0, 31.3, 31.6, 36.7, 60.6, 120.6, 120.8–138.7, 124.9, 171.5; *c*-Et-*t*-Bzl-*t*-$CHCCl_2$: 10.8, 14.4, 22.4, 31.7, 34.7, 37.9, 38.4, 60.8, 118.6–138.1, 122.4, 126.3, 170.7; *c*-Bzl-*t*-Et-*t*-$CHCCl_2$: 10.6, 14.4, 25.5, 32.7, 34.3, 34.5, 60.7, 122.3, 123.5–138.5, 126.9, 171.1. Mass spectrum: *m*/*z* 327 $[M]^+$. Found, %: C 62.64; H 6.37; Cl 22.12. $C_{17}H_{20}Cl_2O_2$. Calculated, %: C 62.38; H 6.11; Cl 21.71. *M* 327.27.

Ethyl 3-(2,2-dichlorovinyl)-2-methyl-2-(2-phenylethyl)cyclopropane-1-carboxylate (VIj). Yield 53% (45% after chromatographic purification), purity 95%. IR spectrum: ν 1621 cm^{-1} (C=C). ^{1}H NMR spectrum, δ, ppm: *c*-Me-*t*-$(CH_2)_2$Ph-*c*-$CHCCl_2$: 1.21 t (3H, $CH_2C\mathbf{H}_3$), 1.33 s (3H, CH_3), 1.59 d (1H, 1-H), 1.78 m and 1.80 m (1H each, CH_2), 2.24 t (1H, 3-H), 2.68 m (1H, C**H**$_2$Ph), 2.78 m (1H, C**H**$_2$Ph), 4.10 q (2H, OCH_2), 5.58 d (1H, CH=), 7.11–7.25 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: *c*-Me-*t*-$(CH_2)_2$Ph-*c*-$CHCCl_2$: 14.4, 17.2, 32.5, 32.9, 33.0, 34.6, 60.8, 122.0, 126.0–141.9, 127.0, 170.8. Mass spectrum: *m*/*z* 327 $[M]^+$. Found, %: C 62.44; H 6.32; Cl 21.97. $C_{17}H_{20}Cl_2O_2$. Calculated, %: C 62.38; H 6.11; Cl 21.71. *M* 327.27.

Ethyl 3-(2,2-dichlorovinyl)-2-methyl-2-phenylcyclopropane-1-carboxylate (VIk). Yield 57% (45% after chromatographic purification), purity 94%. IR spectrum: ν 1621 cm^{-1} (C=C). ^{1}H NMR spectrum, δ, ppm: *c*-Me-*t*-Ph-*c*-$CHCCl_2$: 1.18 t (3H, CH_3), 1.50 s (3H, CH_3), 1 83 d (1H, 1-H), 2.11 t (1H, 3-H), 4.02 q (2H, OCH_2), 6.34 d (1H, CH=), 7.09–7.25 m (5H, Ph); *t*-Me-*c*-Ph-*c*-$CHCCl_2$: 1.18 t (3H, CH_3), 1.25 s (3H, CH_3), 1.84 d (1H, 1-H), 2.08 t (1H, 3-H), 4.05 q (2H, OCH_2), 6.46 d (1H, CH=), 7.02–7.20 m (5H, Ph); *c*-Me-*t*-Ph-*t*-$CHCCl_2$: 1.11 t (3H, CH_3), 1.42 s (3H, CH_3), 1.81 d (1H, 1-H), 2.26 t (1H, 3-H), 4.09 q (2H, OCH_2), 5.65 d (1H, CH=), 7.09–7.23 m (5H, Ph); *t*-Me-*c*-Ph-*t*-$CHCCl_2$: 1.20 t (3H, CH_3), 1.38 s (3H, CH_3), 1.68 d (1H, 1-H), 2.48 t (1H, 3-H), 4.08 q (2H, OCH_2), 5.56 d (1H, CH=), 7.10–7.23 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: *c*-Me-*t*-Ph-*c*-$CHCCl_2$: 14.3, 19.6, 29.7, 31.0, 36.6, 60.5, 120.6–138.9, 123.5, 124.6, 170.5; *t*-Me-*c*-Ph-*c*-$CHCCl_2$: 14.3, 23.54, 31.3, 31.6, 36.7, 60.6, 120.8–138.7, 122.3, 124.8, 171.5; *c*-Me-*t*-Ph-*t*-$CHCCl_2$: 14.4, 21.4, 31.7, 34.7, 38.4, 60.8, 118.6–138.1, 121.6, 126.3, 170.7; *t*-Me-*c*-Ph-*t*-$CHCCl_2$: 14.4, 22.0, 32.7, 34.3, 38.5, 60.9, 120.9–138.9, 124.1, 126.9, 170.8. Mass spectrum: *m*/*z* 229 $[M]^+$. Found, %: C 60.57; H 5.82; Cl 23.36. $C_{15}H_{16}Cl_2O_2$. Calculated, %: C 60.20; H 5.35; Cl 23.74. *M* 299.21.

Assessment of acaricidal activity. Experiments were performed under laboratory conditions on standard sensitive laboratory strains of typhoid fly *Musca domestica L*., rice weevils *Calandra oryzae* L., bean aphides *Aphys fabae* Stock., and twospotted spider mite *Tetranychus urticae* Koch. Tests for juvenile hormone activity were performed on chrysalises of flour beetle *Tenebrio molitor L*. The acute phytotoxicity was studied on hydrangea or cucumber leaves. All experiments were carried out in triplicate.

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