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*Dedicated to Academician of the Russian Academy of Sciences N.S.Zefirov on occasion of his70th anniversary*

# Synthesis of 1-Bromosubstituted Analogs of *cis*-Deltamethrinic and *cis*-Permethrinic Acids

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**Abstract**—In the synthesis of 1-bromosubstituted analogs of *cis*-deltamethrinic and *cis*-permethrinic acids, main components of pyrethroids, the key stage is an intramolecular 1,4-O,C-acyl transfer in reactions of 1-acyloxymethyl-2,2-dibromocyclopropanes with methyllithium.

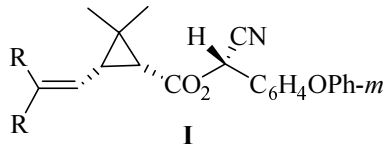
An important groups among synthetic pyrethroids consists of the derivatives of *gem*-dimethylcyclopropane where the unsaturated and ester functions of the molecule are present in the *cis*-orientation [1]. For instance, the cipermethrin (**I**, R = Cl) and deltamethrin (**I**, R = Br) (Scheme 1) are regarded as most efficient insecticides possessing high activity, photostability, and relatively low toxicity with respect to mammals.

Among the versatile stereoselective syntheses of these compounds the following methods may be listed: asymmetrical enantioselective cyclopropanation of 4,4-dihalo-2-methylbuta-1,3-dienes [2], using chiral substrates in intramolecular cyclopropanation [3] or in reactions with sulfur or phosphoruc ylides [4], Faworsky rearrangement with individual enantiomers of 2-chlorocyclobutanones [5], application of chiral lactams [6], enzymatic desymmetrization of 1,4-cyclohexanedione derivatives [7], and also employing natural compounds, e.g., (+)-3-carene [8]. The other general procedures of pyrethroids syntheses [1, 9] involve diazopropane addition to alkynes [10], Claisen rearrangement [11], Grob fragmentation [12], and Grignard reagents addition to 3,3-dimethylcyclopropenes [13].

The goal of this study was synthesis of bromosubstituted pyrethroids based on selective transformations of 1-acyloxymethyl-2,2-dibromo-3,3-dimethylcyclopropanes under the action of methyllithium. The reaction of esters of 2,2-dibromocyclopropylmethanols with methyllithium is known to result in a *cis*-1,4-O,C-migration of the acyl group initiated by the replacement of the *cis*-bromine by lithium (Scheme 2, transitions **II** > **III** > **IV**) [14].

The given scheme proved to be sufficiently effective in transition to 1-bromo-*cis*-hydroxymethyl ketones (**V,** R' = H, $CH_3$). In this connection the extension of that rearrangement to the corresponding 1-acyloxymethyl derivatives of 2,2-dibromo-3,3-dimethylcyclopropane deserved attention. The choice of acyl groups to be transferred from the oxygen to the carbon atom in the small ring allowed for their transformation into substituents at the small ring traditional for pyrethroids (or their analogs).

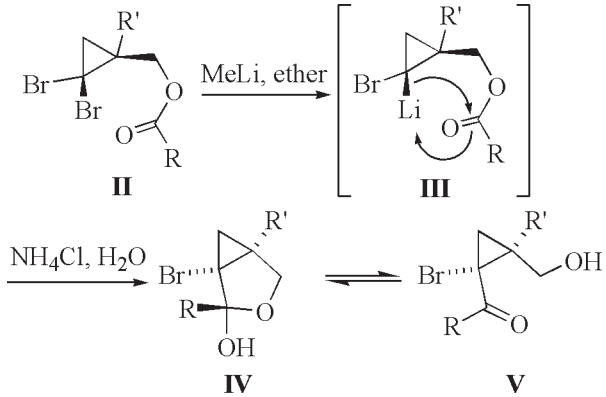
**Scheme 1.**




**I**

R = Cl, Br.

**Scheme 2.**




**II** **III** **IV** **V**

R = alkyl, vinyl, aryl; R' = H, Me.

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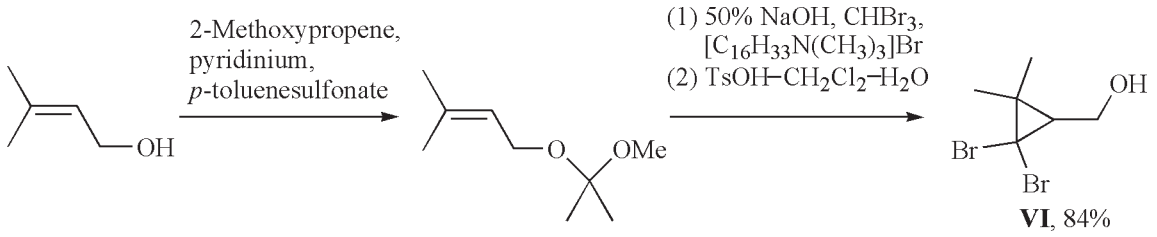
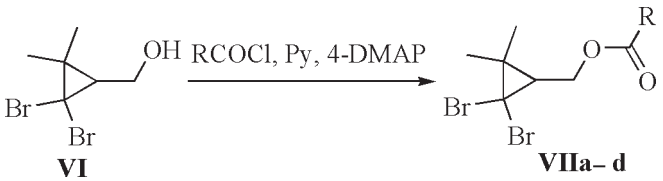
**Scheme 3.**




**VI**, 84%

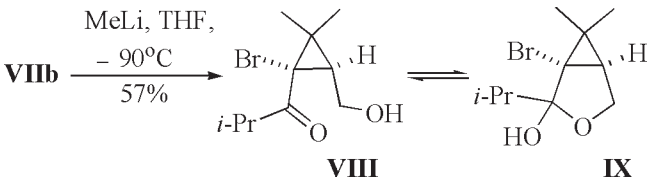
**Scheme 4.**




**VI** **VIIa– d**

**VII**, R = Me, 94% (**a**), *i*-Pr, 100% (**b**), $CHCl_2$, 46% (**c**), $CCl_3$, 88% (**d**).

**Scheme 5.**




**VIII** **IX**

Carbinol **VI** was prepared from accessible prenyl alcohol protected with 2-methoxypropene in the presence of pyridinium *p*-toluenesulfonate. The following stages: dibromocyclopropanation under phase-transfer conditions in the presence of hexadecyl trimethylammonium bromide and removal of the protective group by treating with a catalytic amount of *p*-TsOH resulted in alcohol **VI** in an overall yield 84% * (Scheme 3).

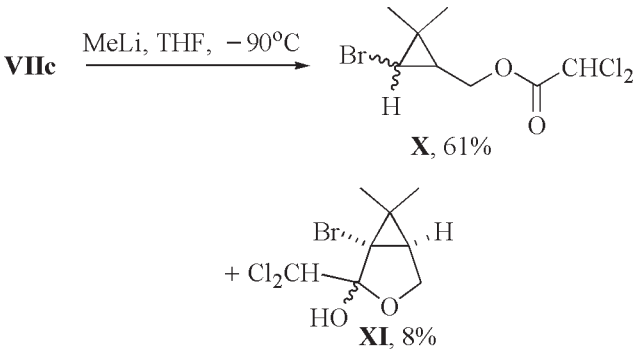
Esters **VIIa–VIId** were obtained from alcohol **VI** and the corresponding acyl halides under standard conditions in the presence 4-dimethylaminopyridine (4-DMAP) as catalyst** (Scheme 4).

The reaction of isobutyrate **VIIb** with methyllithium in a mixture of anhydrous THF and ether*** at the volume ratio 20:1 resulted in a 57% yield of a mixture of mono- and bicyclic forms **VIII** and **IX****** (Scheme 5).

Dichloroacetate **VIIc** under the same conditions (MeLi, THF, –90°C) afforded the expected product of dichloroacetyl group transfer **XI** only in a 8% yield. The main product of this reaction was monobromoester **X** isolated in 61% yield (Scheme 6).

The most important factor governing this direction of the reaction is apparently the great CH-acidity of the dichloroacetyl fragment of the initial dibromide. Therefore the probable sequence of stages leading to monobromoester **X** from dibromide **VIIc** involves the lithiation of the $CBr_2$ fragment of compound **VIIc** followed by intra- or intermolecular proton transfer from the dichloroacetyl group to the generated anionic fragment of the cyclopropyl group. The low stereoselectivity of hydrodebromination of compound **VIIc** also should be noted (the ratio of *cis*- and *trans*-isomers of compound **X** was 1:1.36] that apparently suggests the lack of coordination of the organolithium compound to the dichloroacetyl group prior to the attack on the carbon–bromine bond of the small ring (cf.[14, 17]).

**Scheme 6.**




**X**, 61%

**XI**, 8%

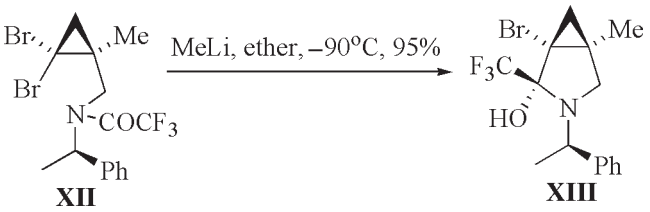
* Before the start of the present investigation three alternative syntheses of compound **VI** were known where prenyl alcohol or its O-derivatives were subjected to dibromocyclopropanation along Makosza reaction. In particular, a direct synthesis from the prenyl alcohol afforded 36 and 67% yield, and the prenyl alcohol with THP-protection furnished compound **VI** in a 65% yield [15].

** Acetate **VIIa** can be obtained also from the prenyl alcohol acetate in a 89% yield [16].

*** Here as ether volume was taken the volume of the ether solution of methyllithium.

**** It should be emphasized that the reproducible results were obtained only at the use of anhydrous THF and ether distilled from sodium just before the experiment. The application of a solvents mixture turned out to be more favorable than using neat ether since in the mixed solvent the formation of carbinol **VI** was prevented which was difficult to separate from the products of acyl transfer.

**Scheme 7.**




**XII** **XIII**

In the case of trichloroacetate **VIId** the main reaction product was alcohol **VI** isolated in 64% yield. Dichloroacetate **VIIc** was obtained as a minor component in a 17% yield.

In analogous reactions 1-acylaminomethyl-2,2-dibromocyclopropane (**XII**) rearranged nearly quantitatively into the corresponding bromoaminomethyl ketone **XIII** even in the case of N-trifluoroacetyl derivative **XII** [17] (Scheme 7), whereas the trifluoroacetate of 2,2-dibromocyclopropylmethanol did not yield products of trifluoroacetyl group transfer [14].

In the final stage of the study the ketoalcohol **XIV** obtained from acetate **VIIa** by reaction with methyllithium was converted into ketoaldehyde **XVI** with the use of pyridinium chlorochromate.*

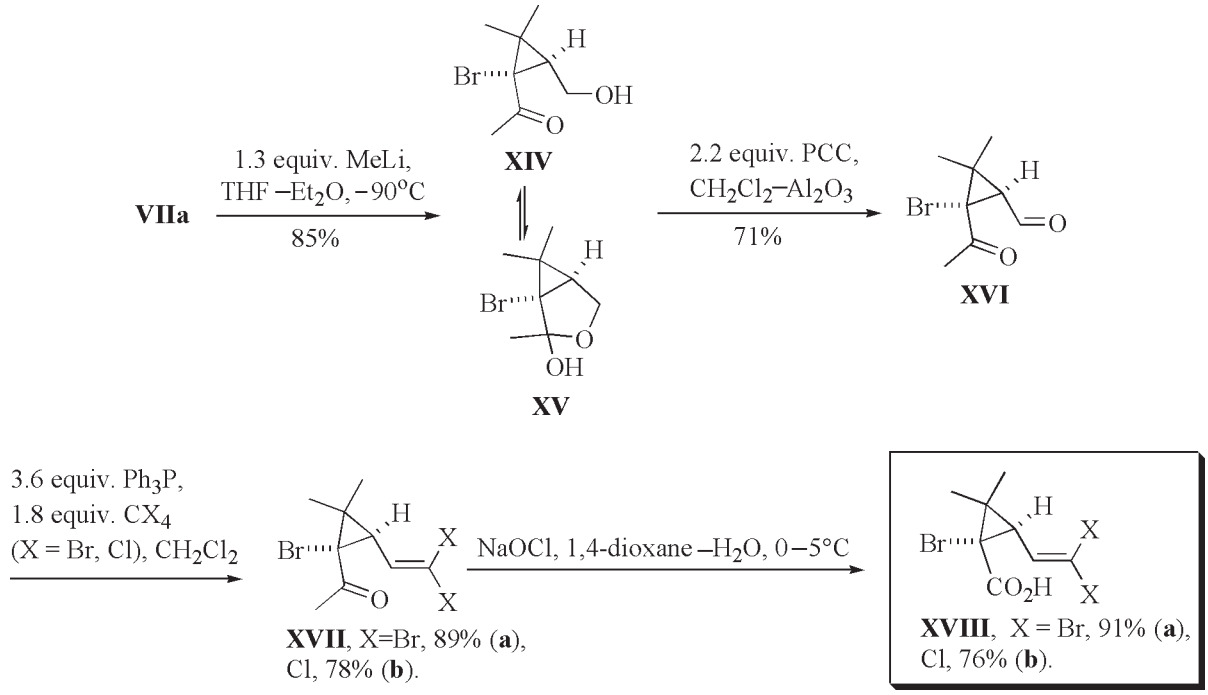
Further reactions of compound **XVI** with carbon tetrabromide or tetrachloride and triphenylphosphine gave rise to dihalovinylcyclopropanes **XVIIa** and **XVIIb** respectively. A haloform reaction of these methyl ketones with sodium hypochlorite in aqueous 1,4-dioxane** afforded 1-bromosubstituted *cis*-deltamethrinic **XVIIIa** and *cis*-permethrinic **XVIIIb** acids in 49 and 36% yields respectively calculated on the initial acetate **VIIa** (Scheme 8).

It should be emphasized in conclusion that this investigation demonstrates one of the opportunities of applying reaction of 1,4-O,C-acyl transfer for the three-carbon rings. The stereoselective building up of a small ring with the desired combination of functional substituents can be employed in the synthesis of versatile practically useful cyclopropanes.

## EXPERIMENTAL

NMR spectra were registered from solution of compounds in deuterochloroform on spectrometers Varian VXR-400, Bruker AC-250, and Bruker A-500 at operating

**Scheme 8.**




* The application as oxidant of pyridinium dichromate on alumina gave similar results.

** Similar result can be obtained with a water solution of potassium hypochlorite, but the complete conversion of initial compounds is reached a lot slower. Mixtures of sodium hydroxide with chlorine or bromine applied to analogous reactions as mild reagents proved to be inefficient in the reactions under study.

frequencies 400, 250 and 500 MHz ($^1$H), and 100, 62.9 and 125 MHz ($^{13}$C). The chemical shifts are presented in the δ scale, ppm, as an internal reference serves residual undeuterated chloroform. The carbon spectra were measured at a wide-band decoupling from protons unless otherwise specified. In most caes DEPT spectra were registered. IR spectra were recorded on a spectrophotometer Perkin Elmer 1600 FTIR from thim films of oily substances and from chloroform solutions of solid samples. Mass spectra and GC-MS measurements (capillary column 25 m long, stationary phase silica gel, initial temperature 60°C, further heating at a rate 10 deg/min) were performed on Finnigan MAT-8430 instrument (ionizing energy 70 eV or chemical ionization with methane was used ). The precision measurement of the substance mass was done on a spectrometer Micromass™ GCT at the mode of direct sample admission. The elemental analyses were carried out on the Carlo-Erba Model 1108 CHNS analyzer. The solvents for the reactions: 1,4-dioxane, hexane, ethyl ether, petroleum ether (bp 40–60°C), pyridine, and dichloromethane of "HPLC grade" or 99+% grade were purchased from Aldrich, Lancaster, Scientific Services Ltd. and were used without further purification except when anhydrous solvents were required. Ethyl ether and THF were dried by boiling with sodium benzophenone ketyl, and dichloromethane was boiled with calcium hydride followed by distillation in the flow of dry nitrogen. Reagents: acetyl chloride, bromoform, hexadecyltrimethylammonium bromide, di- and trichloroacetyl chlorides, 4-dimethylaminopyridine, isobutyryl chloride, 2-methoxypropene, 3-methyl-2-byten-1-ol, tetrabromomethane, pyridinium *p*-toluenesulfonate, and PCC of purity 97–99% were purchased from Avocado, Aldrich and Lancaster and were used without additional purification. The water solution of sodium hypochlorite was prepared as in [18].

The reaction progress was monitored and the purity of compounds obtained was checked by TLC on Aldrich Silica Plates 60 F254 and by $^1$H NMR spectra of the reaction mixtures. The preparative purification of the compounds obtained was carried out by adsorption chromatography on silica gel Matrex Silica 60. The organic solutions were dried over magnesium sulfate and evaporated at 14 mm Hg unless otherwise specified. Melting points of the compounds synthesized were not corrected.

All experiments using substances sensitive to air and moisture were carried out in a flow of dry argon in a glassware preliminary dried at 250°C and cooled in the flow of dry argon. The concentration of methyllithium solutions was determined by standard procedure [19].

**2,2-Dibromo-3,3-dimethylcyclopropylmethanol (VI).** To a solution of 11.8 ml (116 mmol) of prenyl alcohol in 60 ml of anhydrous ether was added at efficient stirring and cooling (0–2°C) 498 mg (1.7 mol%) of pyridinium *p*-toluenesulfonate and a solution of 22.3 ml (0.23 mol) of 2-methoxypropene in 50 ml of anhydrous ether. The reaction mixture was maintained for 50 min at 0°C and then treated with a saturated solution of sodium hydrogen carbonate (50 ml). The organic layer was separated and washed with water (2 × 50 ml), the aqueous extracts were treated with ether (3 × 40 ml). The combined organic solutions were dried over potassium carbonate and concentrated under atmospheric pressure. To the colorless residue (~18.3 g) was added 2.11 g of $[C_{16}H_{33}N(CH_3)_3]Br$, 20.3 ml (0.23 mol) of bromoform, and 50 ml of dichloromethane. To the solution obtained was added dropwise at vigorous stirring within 20 min 62 ml of 50% aqueous solution of sodium hydroxide maintaining the temperature of the reaction mixture below 31°C. On completing the addition the stirring was continued for 19 h more, and then the reaction mixture was poured into 100 ml of cold water. The reaction products were extracted into dichloromethane (3 × 70 ml). The combined organic extracts were washed with a saturated solution of NaCl (2 × 30 ml) and dried. The solvent and residual bromoform were removed in a vacuum. To the viscous oily substance thus obtained was added 100 ml of dichloromethane, 20 ml of water, and 340 mg of *p*-TsOH·$H_2O$. The reaction mixture was stirred for 1 h at 20°C, and 20 ml of saturated solution of sodium hydrogen carbonate was added. The organic layer was separated, the water layer was extracted with 20 ml of dichloromethane. The organic extracts were washed with a saturated solution of NaCl (2 × 10 ml) and dried. On evaporating the extract and fractionating the residue in a vacuum we obtained 25.1 g (84%) of alcohol **VI** [15] as colorless viscous substance which rapidly crystal-lized at –20°C into a white crystalline mass, bp 90–92°C (3 mm Hg), mp 37–38.5°C (hexane), $R_f$ 0.34 (eluent petroleum ether–ethyl acetate, 4:1). IR spectrum (film), cm$^{-1}$: 3500–3000 br.s (OH), 2991 s, 2959 s, 2925 s, 1456 s, 1400 m, 1372 s, 1325 m, 1278 m, 1246 m, 1204 m, 1140 s, 1110 w, 1079 s, 1033 s, 990 m, 912 w, 816 m, 770 s, 751 s, 717 m. $^1$H NMR spectrum (250 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.29 s (3H, Me), 1.44 s (3H, Me), 1.62 t (1H, $^3J$ 7.0), 1.64 br.s (1H, OH), 3.77 d (2H, $CH_2O$, $^3J$ 7.0). $^{13}$C NMR spectrum (62.5 MHz, $CDCl_3$), δ, ppm: 19.5

(Me), 27.3 (Me), 29.0 ($\underline{C}Me_2$), 40.5 (CH), 44.4 ($CBr_2$), 62.0 ($CH_2OH$). Found, %: C 27.99; H 3.85. $C_6H_{10}Br_2O$. Calculated, %: C 27.94; H 3.91.

**Esters of 2,2-dibromo-3,3-dimethylcyclopropylmethanol VIIa–VIId.** To a solution of 2.00 g (7.8 mmol) of alcohol **VI**, 95 mg (10 mol%) of 4-dimethylaminopyridine in 20 ml of pyridine was added 11.6 mmol (1.5 mol-eqiuv) of an appropriate acyl chloride. The reaction mixture was kept for 2 h at room temperature and 10 min at 50°C, and then it was poured into 150 ml of cold water. The reaction product was extracted into ether (3 × 50 ml). The combined organic extracts were washed with 5% water solution of HCl (3 × 50 ml), then with 50 ml of water, and dried. The solvent was distilled off, the crude reaction product was separated from tarry substances by passing through a bed of silica gel. Pure esters **VIIa–VIId** were obtained by this procedure.

**Acetate of 2,2-dibromo-3,3-dimethylcyclopropylmethanol (VIIa).** From 2.00 g of alcohol **VI** and 0.82 ml of acetyl chloride after filtering through a bed of silica gel (52 g, eluent petroleum ether–ethyl acetate, 7:1, $R_f$ 0.56) we obtained 2.19 g (94.4%) of acetate **VIIa** [16] as a colorless oily substance. IR spectrum (film), $cm^{-1}$: 2960 m, 1744 s (C=O), 1461 m, 1370 m, 1235 s, 1154 m, 1084 m, 1034 m, 999 w, 897 w, 809 w, 770 m. $^1H$ NMR spectrum (250 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.28 s (3H, Me), 1.43 s (3H, Me), 1.64 pseudo t (1H, $^3J$ 7.3), 2.10 s (3H, Me), 4.14 d.d (1H, $CH_2O$, $^2J$ 11.9, $^3J$ 7.3), 4.18 d.d (1H, $CH_2O$, $^2J$ 11.9, $^3J$ 7.3). $^{13}C$ NMR spectrum (62.5 MHz, $CDCl_3$), δ, ppm: 19.6 (Me), 20.9 (CH), 27.1 (Me), 28.9 ($\underline{C}Me_2$), 37.0 (CO$\underline{Me}$), 43.4 ($CBr_2$), 63.4 ($CH_2O$), 170.9 (C=O). Chromatomass spectrum, $R_t$ 9.50 min, *m/z* ($I_{rel}$, %): 302 [*M*, $^{81}Br_2$]$^+$ (0.05), 300 [*M*, $^{79}Br+^{81}Br$]$^+$ (0.1), 298 [*M*, $^{79}Br_2$]$^+$ (0.05), 242 [*M* – 60]$^+$ (17), 240 [*M* – 60]$^+$ (34), 238 [*M* – 60]$^+$ (17), 229 (9), 227 (20), 225 (9), 201 (4), 199 (8), 197 (4), 189 (12), 187 (12), 161 (75), 159 (75), 97 (46), 80 (79), 79 (100), 65 (51), 53 (37). Found, %: C 32.04; H 3.87. $C_8H_{12}Br_2O_2$. Calculated, %: C 32.03; H 4.03.

**Isobutyrate of 2,2-dibromo-3,3-dimethylcyclopropylmethanol (VIIb).** From 5.00 g (19.4 mmol) of alcohol **VI** and 3.1 ml (29.1 mmol) of isobutyryl chloride in the presence of 236 mg 4-dimethylaminopyridine after filtering through a bed of silica gel (40 g, eluent petroleum ether–ethyl acetate, 5:1, $R_f$ 0.75) we obtained 6.33 g (99.5%) of isobutyrate **VIIb** as a colorless oily substance. IR spectrum (film), $cm^{-1}$: 2973 s, 2934 s, 2875 s, 1739 s (C=O), 1470 s, 1386 m, 1375 m, 1338 m, 1250 m, 1189 s, 1152 s, 1112 s, 1082 s, 999 m, 913 w, 808 m, 758 m. $^1H$ NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.20 d (6H, CH$\underline{Me}_2$, $^3J$ 7.0), 1.28 s (3H, Me), 1.43 s (3H, Me), 1.66 pseudo t (1H, $^3J$ 7.4), 2.60 septet (1H, C$\underline{H}Me_2$, $^3J$ 7.0), 4.15 d.d (1H, $CH_2O$, $^2J$ 11.9, $^3J$ 7.4), 4.20 d.d (1H, $CH_2O$, $^2J$ 11.9, $^3J$ 7.4). $^{13}C$ NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 18.9 (2Me), 19.6 (Me), 27.1 (Me), 28.9 ($\underline{C}Me_2$), 33.8 (CH), 37.0 (CH), 43.4 ($CBr_2$), 63.1 ($CH_2O$), 176.8 (C=O). Chromatomass spectrum: $R_t$ 9.39 min, *m/z* ($I_{rel}$, %): 330 [*M*, $^{81}Br_2$]$^+$ (0.25), 328 [*M*, $^{79}Br+^{81}Br$]$^+$ (0.5), 326 [*M*, $^{79}Br_2$]$^+$ (0.25), 242 [*M* – 88]$^+$ (4), 240 [*M* – 88]$^+$ (9), 238 [*M* – 88]$^+$ (4), 161 (15), 159 (16), 97 (4), 80 (28), 79 (37), 71 (100), 53 (15). Found, %: C 36.33; H 4.63. $C_{10}H_{16}Br_2O_2$. Calculated, %: C 36.61; H 4.92.

**Dichloroacetate of 2,2-dibromo-3,3-dimethylcyclopropylmethanol (VIIc).** From 2.00 g of alcohol **VI** and 1.12 ml of dichloroacetyl chloride after filtering through a bed of silica gel (60 g, eluent petroleum ether–ethyl acetate, 7:1, $R_f$ 0.47) we obtained 1.32 g (46%) of dichloro-acetate **VIIc** as a colorless oily substance. IR spectrum (film), $cm^{-1}$: 2994 m, 2962 m, 2928 m, 1767 s (C=O), 1457 s, 1391 w, 1376 m, 1352 m, 1300 s, 1162 s, 1112 w, 1083 m, 1043 w, 997 m, 816 s, 771 m, 727 m. $^1H$ NMR spectrum (500 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.33 s (3H, Me), 1.47 s (3H, Me), 1.74 pseudo t (1H, $^3J$ 7.6), 4.32 d.d (1H, $CH_2O$, $^2J$ 11.9, $^3J$ 7.6), 4.48 d.d (1H, $CH_2O$, $^2J$ 11.9, $^3J$ 7.6), 6.01 s (1H, $CHCl_2$). $^{13}C$ NMR spectrum (125 MHz, $CDCl_3$), δ, ppm: 19.7 (Me), 27.0 (Me), 29.4 ($\underline{C}Me_2$), 36.4 (CH), 42.3 ($\underline{C}Br_2$), 64.0 ($CHCl_2$), 66.5 ($CH_2O$), 164.3 (C=O). Chromatomass spectrum: $R_t$ 12.23 min, *m/z* ($I_{rel}$, %): 242 [*M* – 129, $^{81}Br_2$]$^+$ (6), 240 [*M* – 129, $^{79}Br+^{81}Br$]$^+$ (14), 238 [*M* – 129, $^{79}Br_2$]$^+$ (6), 229 (18), 227 (36), 225 (17), 201 (4), 199 (8), 197 (4), 161 (54), 159 (53), 83 (59), 80 (75), 79 (100), 53 (27). Found, %: C 26.32; H 2.77. $C_8H_{10}Br_2Cl_2O_2$. Calculated, %: C 26.05; H 2.73.

**Trichloroacetate of 2,2-dibromo-3,3-dimethylcyclopropylmethanol (VIId).** From 2.00 g of alcohol **VI** and 1.30 ml of trichloroacetyl chloride after filtering through a bed of silica gel (50 g, eluent petroleum ether–ethyl acetate, 6:1, $R_f$ 0.67) we obtained 2.74 g (88%) of trichloro-acetate VIId as a colorless powder, mp 46–47.5°C. IR spectrum ($CHCl_3$), $cm^{-1}$: 2964 m, 1765 s, 1457 m, 1392 w, 1376 w, 1153 m, 1084 m, 994 m, 845 m, 828 m, 682 m, 669 m. $^1H$ NMR spectrum (500 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.33 s (3H, Me), 1.45 s (3H, Me), 1.76 pseudo-t (1H, $^3J$ 7.6), 4.36 d.d (1H, $CH_2O$, $^2J$ 11.6, $^3J$ 7.6), 4.59 d.d (1H, $CH_2O$, $^2J$ 11.6, $^3J$ 7.6).

$^{13}$C NMR spectrum (125 MHz, $CDCl_3$), δ, ppm: 19.8 (Me), 27.0 (Me), 29.6 ($\underline{C}Me_2$), 36.2 (CH), 42.0 ($CBr_2$), 68.3 ($CH_2O$), 89.6 ($CCl_3$), 161.8 (C=O). Chromatomass spectrum, $R_t$ 12.69 min, *m/z* ($I_{rel}$, %): 242 [$M$ – 163, $^{81}Br_2$]$^+$ (7), 240 [$M$ – 163, $^{79}Br$+$^{81}Br$]$^+$ (14), 238 [$M$ – 163, $^{79}Br_2$]$^+$ (7), 229 (18), 227 (38), 225 (19), 201 (5), 199 (10), 197 (5), 161 (60), 159 (62), 119 (60), 117 (56), 97 (18), 80 (86), 79 (100), 53 (26). Found, %: C 24.06; H 2.26. $C_8H_9Br_2Cl_3O_2$. Calculated, %: C 23.82; H 2.25.

**2-Bromo-2*c*-isobutyryl-3,3-dimethylcyclopropyl-1*r*-methanol (VIII) and 1-bromo-2-isopropyl-6,6-dimethyl-3-oxabicyclo[3.1.0]hexan-2-ol (IX).** To a solution of 3.0 g (9.2 mmol) of isobutyrate **VIIb** in 60 ml of anhydrous THF was added dropwise within 5 min 6.5 ml of 1.87 M methyllithium solution in ether at –95°C. The reaction mixture was maintained for 30 min at –90°C, then within 40 min the temperature of the mixture was raised to 0°C, and gradually 25 ml of saturated $NH_4Cl$ solution was added. The organic layer was separated, the water layer was extracted with ether (3 × 15 ml). The combined organic solutions were washed with 10 ml of water and dried. On distilling off the solvent the residue (2.09 g) was subjected to chromatography on silica gel (150 g, eluent petroleum ether–ethyl acetate, 4:1, $R_f$ 0.32).We isolated 1.31 g (57%) of a mixture of isomers **VIII** and **IX** in a ratio 2:1 as colorless viscous oily substance. IR spectrum (film), cm$^{-1}$: 3700–3100 br.s (OH), 2973 s, 2876 s, 1694 s (C=O), 1466 m, 1381 m, 1340 m, 1293 w, 1255 w, 1226 w, 1185 w, 1161 w, 1122 m, 1095 m, 1024 s, 968 w, 942 w, 888 w, 843 m, 813 w, 756 w, 732 w. $^1$H NMR spectrum (500 MHz, $CDCl_3$) of ketoalcohol **VIII** in a mixture with compound **IX**, δ, ppm (*J*, Hz): 1.11 d (3H, CH$\underline{Me}_2$, $^3J$ 6.9), 1.12 s (3H, Me), 1.21 d (3H, CH$\underline{Me}_2$, $^3J$ 6.6), 1.50 s (3H, Me), 1.72 d.d (1H, $^3J$ 9.6, $^3J$ 9.4), 2.59 br.s (1H, OH), 3.30 q.q (1H, C$\underline{H}Me_2$, $^3J$ 6.9, $^3J$ 6.6), 3.77 d.d (1H, $CH_2O$, $^2J$ 11.6, $^3J$ 9.4), 3.90 d.d (1H, $CH_2O$, $^2J$ 11.6, $^3J$ 9.6). $^1$H NMR spectrum (500 MHz, $CDCl_3$) of hemiketal **IX** from the mixture with compound **VIII**, δ, ppm (*J*, Hz): 1.01 d (3H, CH$\underline{Me}_2$, $^3J$ 7.0), 1.18 d (3H, CH$\underline{Me}_2$, $^3J$ 7.2), 1.29 s (3H, Me), 1.38 s (3H, Me), 1.56 d (1H, $^3J$ 3.7), 2.02 q.q (1H, C$\underline{H}Me_2$, $^3J$ 7.2, $^3J$ 7.0), 2.86 br.s (1H, OH), 3.77 d (1H, *endo*-H–C–O, $^2J$ 9.2), 4.23 d.d (1H, *exo*-H–C–O, $^2J$ 9.2, $^3J$ 3.7). $^{13}$C NMR spectrum (125 MHz, $CDCl_3$) of mixtures of isomers **VIII** and **IX**, δ, ppm: 15.5, 16.9, 17.1, 18.4, 19.1, 20.1, 26.3, 26.9 ($\underline{C}Me_2$), 28.2, 29.1 ($\underline{C}Me_2$), 34.9, 35.9, 39.1, 40.6 (CBr), 42.6, 49.8 (CBr), 59.6 ($CH_2O$), 64.9 ($CH_2O$), 106.5 (C-semiketal), 210.6 (C=O). Mass spectrum of chemical ionization with methane, *m/z* ($I_{rel}$, %): 251 [$M$H, $^{81}$Br]$^+$ (11), 249 [$M$H, $^{79}$Br]$^+$ (12), 219 (54), 217 (28), 209 (66), 197 (100), 182 (39), 152 (19), 139 (18), 71 (7). Found: [$M$H]$^+$ 251.0474. $C_{10}H_{18}{}^{81}BrO_2$. Calculated: $M$H 251.0470.

**Dichloroacetate of 2-bromo-3,3-dimethylcyclopropylmethanol (X) and 1-bromo-2-dichloromethyl-6,6-dimethyl-3-oxabicyclo[3.1.0]hexan-2-ol (XI).** To a solution of 500 mg (1.36 mmol) of dichloroacetate **VIIc** in 16 ml of anhydrous THF was added dropwise within 5 min 1.3 ml of 1.40 M methyllithium solution in ether at –92°C. The solution self-cooled to–105°C, it was warmed to –95°C and stirred at this temperature for 30 min. Then the temperature of the mixture was raised to –70°C, and 5 ml of saturated solution of $NH_4Cl$ was quickly added thereto. The organic layer was separated, the water layer was extracted with ether (3 × 5 ml). The combined organic solutions were washed with 5 ml of water and dried. The solvent was distilled off, and the residue (359 mg) was subjected to chromatography on silica gel (20 g, eluent petroleum ether–ethyl acetate, 3:1). We isolated 241 mg (61%) of dichloroacetate **X** (ratio of *cis*- and *trans*-isomers 1:1.36, $R_f$ 0.70) as colorless oily substance and 31 mg (8%) of compound **XI** (ratio of *endo*- and *exo*-isomers 1.7:1, $R_f$ 0.40) as colorless powder, mp 115–117°C (decomp.).

Dichloroacetate **X**. IR spectrum (film), cm$^{-1}$: 2959 m, 2926 m, 1764 s (C=O), 1457 m, 1292 s, 1165 s, 987 m, 816 m. $^1$H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.20 s (6H, 2Me), 1.30 s (6H, 2Me), 1.42 m (2H), 2.80 d (1H, *trans*-HCBr, $^3J$ 4.0), 3.03 d (1H, *cis*-HCBr, $^3J$ 7.6), 4.14–4.49 m (4H, $2CH_2O$), 5.97 s (2H, $2CHCl_2$). $^{13}$C NMR spectrum (125 MHz $CDCl_3$) δ, ppm: 17.3, 19.7, 24.2, 24.3, 26.7, 27.0, 31.4, 32.8, 34.0, 36.3, 64.1, 64.2, 66.8, 67.0, 164.4 (C=O). Found: [$M$]$^+$ 289.9301. $C_8H_{11}{}^{81}Br^{35}Cl_2O_2$. Calculated: $M$ 289.9299.

*endo*-Isomer **XI** from a mixture with *exo*-isomer **XI**. $^1$H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.36 s (3H, Me), 1.43 s (3H, Me), 1.78 d (1H, $^3J$ 4.0), 3.76 br.s (1H, OH), 3.88 d (1H, *endo*-H–C–O, $^2J$ 9.2), 4.38 d.d (1H, *exo*-H–C–O, $^2J$ 9.2, $^3J$ 4.0), 5.82 s (1H, $CHCl_2$). $^{13}$C NMR spectrum (125 MHz, $CDCl_3$), δ, ppm: 15.4 (Me), 27.0 ($\underline{C}Me_2$), 27.8 (Me), 37.3 (CH), 49.7 (CBr), 66.6 ($CH_2O$), 73.7 ($CHCl_2$), 103.5 (C-hemiketal).

*exo*-Isomer **XI** from a mixture with *endo*-isomer. $^1$H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.38 s (3H, Me), 1.42 s (3H, Me), 1.84 d (1H, $^3J$ 4.3), 3.40 br.s (1H, OH), 4.03 d (1H, *endo*-H–C–O, $^2J$ 8.9), 4.54 d.d (1H, *exo*-H-C-O, $^2J$ 8.9, $^3J$ 4.3), 6.27 s (1H, $CHCl_2$). $^{13}$C NMR spectrum (125 MHz, $CDCl_3$), δ, ppm:

15.5 (Me), 26.2 (C$Me_2$), 27.6 (Me), 36.5 (CH), 48.9 (CBr), 70.6 ($CH_2O$), 79.8 ($CHCl_2$), 106.8 (C-hemiketal). Mixture of *endo*- and *exo*-isomers **XI**. IR spectrum ($CHCl_3$), $cm^{-1}$: 3600–3100 br.s (OH), 2926 m, 1438 m, 1261 w, 1105 m, 715 m, 692 m, 669 C, 638 m. Found: $[M]^+$ 287.9325. $C_8H_{11}{}^{79}Br^{35}Cl_2O_2$. Calculated: *M* 287.9319.

**Reaction of trichloroacetate of 2,2-dibromo-3,3-dimethylcyclopropylmethanol (VIId) with methyllithium.** To a solution of 250 mg (0.62 mmol) of trichloroacetate **VIId** in 8 ml of anhydrous THF was added dropwise within 3 min 0.43 ml of 1.88 M methyllithium solution in ether at –95°C. The content of the flask was kept for 35 min at –90°C, and then 2 ml of saturated $NH_4Cl$ solution was quickly added. The organic layer was separated, the water layer was extracted with ether (3 × 5 ml). The combined organic solutions were washed with 5 ml of water and dried. On removing the solvent the residue (185 mg) was subjected to chromatography on silica gel (20 g, eluent petroleum ether–ethyl acetate, 5:1); we obtained 40 mg (18%, $R_f$ 0.66) of dichloroacetate **VIIc** as colorless oily substance and 102 mg (64%, $R_f$ 0.18) of alcohol **VI** as a white powder. Analytical and spectral characteristics of compounds **VI** and **VIIc** were identical to those described above.

**2*c*-Acetyl-2-bromo-3,3-dimethylcyclopropylmethanol-1*r* (XIV) and 1-bromo-2-methyl-6,6-dimethyl-3-oxabicyclo[3.1.0]hexan-2-ol (XV).** To a solution of 5.19 g (17.3 mmol) of acetate **VIIa** in a mixture of anhydrous 120 ml of THF and 6 ml of ether was added dropwise within 10 min 17.3 ml of 1.30 M methyllithium solution in ether at –92°C. The solution obtained was maintained for 40 min at –90°C, then within 30 min the temperature of the mixture was raised to 0°C, and gradually 50 ml of saturated $NH_4Cl$ solution was added. The organic layer was separated, the water layer was extracted with erther (2 × 20 ml). The combined ether extracts were washed with 20 ml of water, dried, and evaporated. The residue (~4.5 g) was subjected to chromatography on silica gel (100 g, eluent petroleum ether–ether, 2:3, $R_f$ 0.29); we obtained 3.24 g (85%) of a mixture of isomeric compounds **XIV** and **XV** in a ratio 0.6:1.0 as a colorless fine crystalline powder, mp 64–67°C (hexane). Ketoalcohol **XIV** from the mixture with hemiketal **XV**. $^1$H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.15 s (3H, Me), 1.47 s (3H, Me), 1.68 d.d (1H, $^3J$ 9.9, $^3J$ 6.7), 2.43 s (3H, Me), 2.65 d.d (1H, OH, $^3J$ 3.7, $^3J$ 3.4), 3.65 d.d.d (1H, $CH_2O$, $^2J$ 12.4, $^3J$ 9.9, $^3J$ 3.4), 3.85 d.d.d (1H, $CH_2O$, $^2J$ 12.4, $^3J$ 6.7, $^3J$ 3.7). $^1$H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm (*J*, Hz) of hemiketal **XV** from the mixture with ketoalcohol **XIV**: 1.26 s (3H, Me), 1.33 s (3H, Me), 1.52 s (3H, Me), 1.61 d (1H, $^3J$ 3.5), 2.82 br.s (1H, OH), 3.77 d (1H, *endo*-H–C–O, $^2J$ 9.2), 4.23 d.d (1H, *exo*-H–C–O, $^2J$ 9.2, $^3J$ 3.5).

Mixture of isomers **XIV** and **XV**. IR spectrum (film), $cm^{-1}$: 3600–3100 br.s (OH), 3007 s, 2986 s, 2956 s, 2877 m, 1705 m (C=O), 1460 m, 1444 m, 1405 m, 1378 s, 1340 m, 1224 m, 1174 s, 1124 m, 1088 m, 1075 m, 1042 s, 994 m, 966 s. $^{13}$C NMR spectrum (125 MHz, $CDCl_3$), δ, ppm: 14.5, 16.2, 21.8, 26.0 (C$Me_2$), 26.1, 27.0 (C$Me_2$), 28.0, 29.1, 34.2, 40.9, 50.0 (CBr), 55.3 (CBr), 59.6 ($CH_2O$), 65.3 ($CH_2O$), 104.2 (C-hemiketal), 202.9 (C=O). Mass spectrum, *m/z* ($I_{rel}$, %): 192 [*M* – $CH_2O$, $^{81}$Br]$^+$ (19), 190 [*M* – $CH_2O$, $^{79}$Br]$^+$ (19), 191 [*M* – 31, $^{81}$Br]$^+$ (74), 189 [*M* – 31, $^{79}$Br]$^+$ (90), 159 (11), 111 (26), 110 (100), 109 (17), 95 (11), 81 (32), 79 (17), 67 (14). Found, %: C 43.5; H 5.8. $C_8H_{13}BrO_2$. Calculated, %: C 43.46; H 5.93.

**2*c*-Acetyl-2-bromo-1*r*-formyl-3,3-dimethylcyclopropane (XVI).** A solution of 784 mg (3.6 mmol) of a mixture of isomers **XIV** and **XV** in 7 ml of anhydrous dichloromethane was added dropwise within 5 min to 840 mg (3.9 mmol) of a stirred dispersion of pyridinium chlorochromate (PCC) and 4.6 g of aluminum oxide in 18 ml of anhydrous dichloromethane under an argon atmosphere. The arising mixture was kept for 4 h at room temperature, and then again 840 mg of PCC was added, and the stirring was continued for 10 h more. Then the solvent was removed, the black solid residue was transferred on a glass frit with 15 g of silica gel, and the product was eluted from the filter with 100 ml of dichloromethane under a slightly reduced pressure of a water-jet pump. On distilling off the solvent we obtained 552 mg (71%) of ketoaldehyde **XVI** as a colorless oily substance which was crystallized from a mixture ether–hexane, 1:1, to get a colorless crystalline compound, mp 66–67°C, $R_f$ 0.48 (eluent petroleum ether–ethyl acetate, 8:1). IR spectrum (film), $cm^{-1}$: 3020 s, 1706 br.s (CH=O, C=O), 1422 w, 1379 w, 1359 w, 1257 w, 1215 s, 1125 m, 1030 w, 985 w, 928 w, 757 s, 669 m. $^1$H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.44 s (3H, Me), 1.56 s (3H, Me), 2.08 d (1H, C$H$CHO, $^3J$ 5.5), 2.49 s (3H, COMe), 9.49 d (1H, CH=O, $^3J$ 5.5). $^{13}$C NMR spectrum (125 MHz, $CDCl_3$), δ, ppm: 16.2 (Me), 26.2 (Me), 28.4 (CH), 33.5 (C$Me_2$), 48.0 (CO$Me$), 54.1 (CBr), 196.7 (CH=O), 199.5 (C=O). Chromatomass spectrum: $R_t$ 8.29 min, *m/z* ($I_{rel}$, %): 220 [*M*, $^{81}$Br]$^+$ (0.5), 218 [*M*, $^{79}$Br]$^+$ (0.5), 191 [*M* – 29, $^{81}$Br]$^+$ (43), 189 [*M* –

29, $^{79}Br]^+$ (45), 177 [$M$ – 43, $^{81}Br]^+$ (9), 175 [$M$ – 43, $^{79}Br]^+$ (9), 139 (3), 110 (100), 95 (38), 81 (29), 67 (46), 51 (31). Found, %: C 44.14; H 4.91. $C_8H_{11}BrO_2$. Calculated, %: C 43.86; H 5.06.

**1*c*-Acetyl-1-bromo-2*r*-(2,2-dibromovinyl)-3,3-dimethylcyclopropane (XVIIa).** To a solution of 2.44 g (9.3 mmol) of triphenylphosphine in 14 ml of anhydrous dichloromethane cooled to 0°C was added under an argon atmosphere 1.54 g (4.7 mmol) of tetrabromomethane. In 15 min to the formed orange solution was added dropwise within 5 min a solution of 566 mg (2.6 mmol) of ketoaldehyde **XVI** in 6 ml of anhydrous dichloromethane. The content of the flask was kept for 30 min at 20°C and then treated with 7 ml of water. The organic layer was separated, the reaction products were extracted from the water layer with dichloromethane (2 × 5 ml). The combined organic solutions were washed with 5 ml of saturated solution of NaCl and dried. On removing the solvent the residue was subjected to chromatography on silica gel (35 g, eluent petroleum ether–ethyl acetate, 23:1>15:1, $R_f$ 0.45) to isolate 860 mg (89%) of methyl ketone **XVIIa** as a colorless oily substance that crystallized after standing overnight at 5°C into a colorless crystalline mass, mp 29–30°C. IR spectrum (film), cm$^{-1}$: 3061 m, 2958 m, 2926 m, 1708 s (C=O), 1457 m, 1419 w, 1376 m, 1354 m, 1301 w, 1257 m, 1198 m, 1145 m, 1110 m, 1026 w, 988 m, 889 m, 836 w, 768 m, 721 w, 645 w. $^1$H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm ($J$, Hz): 1.18 s (3H, Me), 1.56 s (3H, Me), 2.15 d (1H, C<u>H</u>–CH=, $^3J$ 8.2), 2.45 s (3H, COMe), 6.66 d (1H, CH=, $^3J$ 8.2). $^{13}$C NMR spectrum (125 MHz, $CDCl_3$), δ, ppm: 16.5 (Me), 26.4 (Me), 30.1 (CH), 31.3 (<u>C</u>Me$_2$), 43.8 (CO<u>Me</u>), 51.1 (CBr), 91.1 (=CBr$_2$), 132.6 (CH=), 201.0 (C=O). Chromato-mass spectrum: $R_t$ 11.63 min, $m/z$ ($I_{rel}$, %): 378 [$M$, $^{81}Br_3]^+$ (1), 376 [$M$, $^{79}Br+^{81}Br_2]^+$ (2), 374 [$M$, $^{79}Br_2+^{81}Br]^+$ (2), 372 [$M$, $^{79}Br_3]^+$ (1), 297 (23), 295 (46), 293 (23), 254 (15), 252 (29), 250 (15), 239 (14), 237 (18), 235 (9), 215 (29), 213 (27), 187 (16), 173 (39), 171 (40), 158 (20), 135 (14), 106 (17), 92 (80), 91 (100), 77 (31), 65 (30), 51 (42). Found, %: C 28.94; H 2.83. $C_9H_{11}Br_3O$. Calculated, %: C 28.83; H 2.96.

**1*c*-Acetyl-1-bromo-2*r*-(2,2-dichlorovinyl)-3,3-dimethylcyclopropane (XVIIb).** To a solution of 1.44 g (5.5 mmol) of triphenylphosphine in 5 ml of anhydrous dichloromethane cooled to 0°C was added under an argon atmosphere 2 ml of $CCl_4$. In 15 min to the formed solution was added dropwise within 5 min a solution of 300 mg (1.37 mmol) of ketoaldehyde **XVI** in 3 ml of anhydrous dichloromethane. The stirring was continued for 1.5 h at 20°C, then 5 ml of water was added. The organic layer was separated, the reaction products were extracted from the water layer with dichloromethane (2 × 5 ml). The combined organic solutions were washed with 5 ml of saturated solution of NaCl and dried. On removing the solvent the residue was subjected to chromatography on silica gel (15 g, eluent petroleum ether–ether, 25:1, $R_f$ 0.27) to obtain 306 mg (78%) of methyl ketone **XVIIb** as colorless oily substance. IR spectrum (film), cm$^{-1}$: 3075 m, 2960 m, 2928 m, 1709 s (C=O), 1611 m, 1458 m, 1377 s, 1355 s, 1304 m, 1256 s, 1198 s, 1152 m, 1111 m, 990 m, 911 m, 811 m, 732 w, 702 w. $^1$H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm ($J$, Hz): 1.17 s (3H, Me), 1.55 s (3H, Me), 2.23 d (1H, C<u>H</u>–CH=, $^3J$ 8.6), 2.44 s (3H, COMe), 6.13 d (1H, CH=, $^3J$ 8.6). $^{13}$C NMR spectrum (125 MHz, $CDCl_3$), δ, ppm: 16.4 (Me), 26.4 (Me), 30.1 (CH), 31.3 (<u>C</u>Me$_2$), 40.9 (CO<u>Me</u>), 51.3 (CBr), 122.2 (=CCl$_2$), 124.0 (CH=), 201.0 (C=O). Mass spectrum, $m/z$ ($I_{rel}$, %): 290 [$M$, $^{37}Cl_2+^{81}Br]^+$ (0.07), 288 [$M$]$^+$ (0.6), 286 [$M$]$^+$ (2), 284 [$M$, $^{35}Cl_2+^{79}Br]^+$ (1), 207 (61), 205 (100), 164 (6), 162 (21), 147 (38), 129 (3), 127 (33), 91 (48), 86 (75), 84 (90). Found: [$M$]$^+$ 285.9351. $C_9H_{11}{}^{81}Br^{35}Cl_2O$. Calculated: $M$ 285.9350.

**1-Bromo-2*c*-(2,2-dibromovinyl)-3,3-dimethylcyclopropane-1*r*-carboxylic acid (XVIIIa).** To a solution of 494 mg (1.3 mmol) of methyl ketone **XVIIa** in a mixture of 9 ml of 1,4-dioxane and 2 ml of water at cooling to 0°C was added dropwise 4.4 ml of freshly prepared sodium hypochlorite solution. The reaction mixture was stirred for 1.5 h at 0–5°C, then 5 ml of saturated water solution of sodium sulfite and 5 ml of water was added. The solution obtained was treated with chloroform (2 × 10 ml), the water layer was acidified with cold 10% aqueous HCl till pH 1, and the reaction products were extracted with ether (3 × 10 ml). The combined ether extracts were washed with 5 ml of saturated solution of NaCl, dried, and evaporated. We obtained 451 mg (91%) of *trans*-1-bromodeltamethrinic acid (**XVIIIa**) as a colorless fine crystalline powder, mp 123–128°C (decomp., hexane). IR spectrum ($CHCl_3$), cm$^{-1}$: 3500–2000 br.s ($CO_2H$), 2971 C, 2667 C, 1692 C (C=O), 1443 m, 1418 C, 1392 m, 1377 m, 1299 C, 1271 C, 1223 C, 1108 m, 999 m, 954 m, 905 C, 868 m, 840 m, 810 m, 760 C. $^1$H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm ($J$, Hz): 1.30 C (3H, Me), 1.57 C (3H, Me), 2.22 d (1H, C<u>H</u>–CH=, $^3J$ 7.9), 6.65 d (1H, CH=, $^3J$ 7.9). $^{13}$C NMR spectrum (125 MHz, $CDCl_3$), δ, ppm: 16.8 (Me), 26.7 (Me), 31.7 (<u>C</u>Me$_2$), 41.5 (CBr), 44.0 (CH), 92.3 (=CBr$_2$), 131.9 (CH=), 172.1 ($CO_2H$). Found,

%: C 25.32; H 2.53. $C_8H_9Br_3O_2$. Calculated, %: C 25.50; H 2.41.

**1-Bromo-2*c*-(2,2-dichlorovinyl)-3,3-dimethylcyclopropane-1*r*-carboxylic acid (XVIIIb).** To a solution of 150 mg (0.5 mmol) of methyl ketone **XVIIb** in a mixture of 3.5 ml of 1,4-dioxane and 1.2 ml of water at cooling to 0°C was added dropwise 1.8 ml of freshly prepared sodium hypochlorite solution. The reaction mixture was kept for 1.5 h at 0–5°C, then 2 ml of saturated water solution of sodium sulfite and 5 ml of water was added. The reaction mixture was treated with chloroform (2 × 5 ml), the water layer was acidified with cold 10% aqueous HCl till pH 1, and the carboxylic acid was extracted with ether (3 × 10 ml). The combined ether extracts were washed with 5 ml of saturated solution of NaCl and dried. On removing the solvent in a vacuum we obtained 115 mg (76%) of *trans*-1-bromopermethrinic acid (**XVIIIb**) as a colorless fine crystalline powder, mp 117–118°C (decomp., hexane). IR spectrum ($CHCl_3$), $cm^{-1}$: 3600–2300 br.s ($CO_2H$), 3082 s, 2976 s, 2938 s, 2669 m, 1691 C (C=O), 1612 m, 1463 m, 1446 m, 1421 s, 1378 m, 1302 s, 1274 s, 1227 s, 1001 m, 954 m, 919 s, 844 m, 832 s, 758 s, 653 m. $^1H$ NMR spectrum (500 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.29 s (3H, Me), 1.57 s (3H, Me), 2.30 d (1H, C<u>H</u>–CH=, $^3J$ 8.5), 6.11 d (1H, CH=, $^3J$ 8.5), 7.42 br.s (1H, $CO_2H$). $^{13}C$ NMR spectrum (125 MHz, $CDCl_3$), δ, ppm: 16.7 (Me), 26.6 (Me), 31.8 (<u>C</u>$Me_2$), 41.1 (CH), 41.7 (CBr), 123.29 (CH=), 123.31 (=$CCl_2$), 172.5 ($CO_2H$). Found, %: C 33.12; H 3.38. $C_8H_9BrCl_2O_2$. Calculated, %: C 33.37; H 3.15.

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