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Synthesis of Dicyclopropanes from 4,7,7-Trimethyl-3-oxabicyclo[4.1.0]hept-4-en-2-one

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Abstract—New optically active dicyclopropanes were synthesized on the basis of transformation products of 4,7,7-trimethyl-3-oxabicyclo[4.1.0]hept-4-en-2-one using dichlorocarbene or sulfoxonium ylide in the key cyclopropanation stages.

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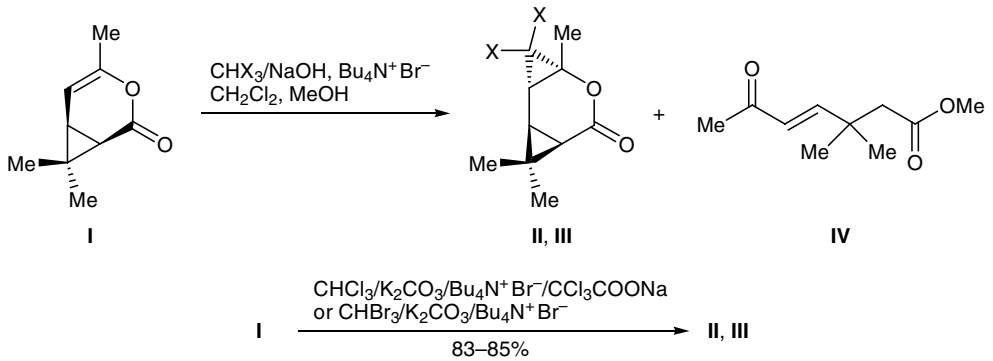
Cyclopropane ring is a structural fragment of many biologically active compounds, including highly efficient insecticides and incest growth and development regulators. In the recent years, strong physiological activity has been revealed in the series of conjugated polycyclopropane derivatives, and interest in these compounds has increased considerably [1]. Almost all known syntheses of such polycyclopropanes are based on a combination of olefination and Simmons–Smith cyclopropanation.

The goal of the present study was to develop synthetic routes to new polycyclopropanes on the basis of 2,2-dimethylcyclopropanecarboxylic acid derivatives which exhibit strong biological activity [2]. As starting material we used 4,7,7-trimethyl-3-oxabicyclo[4.1.0]-hept-4-en-2-one (**I**) which is readily available via successive transformations of (+)-3-carene [3].

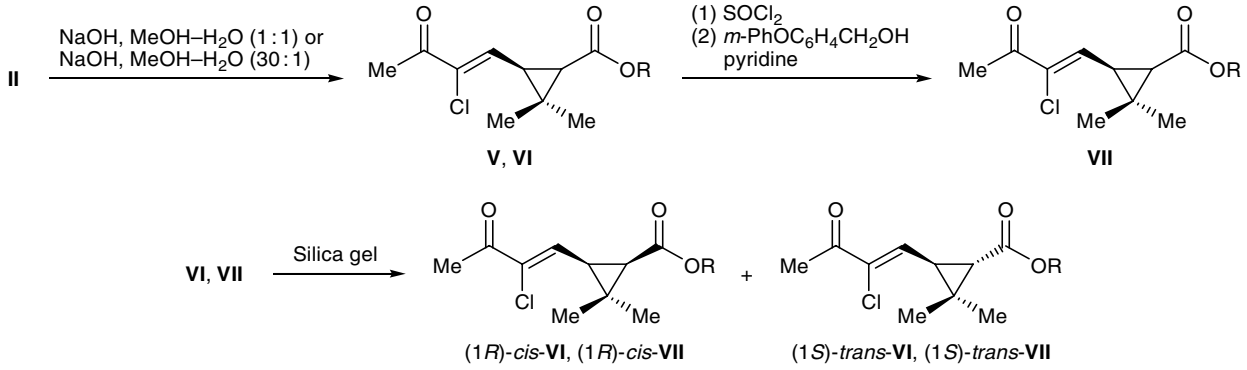
It was reported previously that cyclopropanation of unsaturated lactone **I** with dichlorocarbene generated from $PhHgCCl_3$ [4] or by the Makosza reaction under temperature-controlled conditions ($CHCl_3$/NaOH/$Et_3BzlN^+Cl^-$, 30°C) [5] leads to the formation in both cases of 5,5-dichloro-4,8,8-trimethyl-3-oxatricyclo-[5.1.0.$0^{4,6}$]octan-2-one (**II**) in a good yield. However, the yield of the corresponding dibromo derivative **III** in the cyclopropanation of **I** with dibromocarbene generated under analogous conditions ($CHBr_3$/NaOH/$Et_3BzlN^+Cl^-$, 30°C) did not exceed 55% [5]. We have found that the reaction performed above 30°C is accompanied by formation of a considerable amount (up

Scheme 1.



II, X = Cl; **III**, X = Br.

Scheme 2.



V, R = H; **VI**, R = Me; **VII**, R = *m*-$PhOC_6H_4CH_2$.

to 65%) of methyl 3,3-dimethyl-6-oxohept-4-enoate (**IV**) [6] in addition to compound **II** or **III** (Scheme 1). When dihalocarbene is generated by the action of K_2CO_3 on CHX_3, the corresponding dicyclopropane **II** or **III** is formed as the only product in a high yield.

Alkaline hydrolysis of the lactone ring in **II** in aqueous methanol, depending on the solvent ratio, gives 3-(2-chloro-3-oxobut-1-en-1-yl)-2,2-dimethylcyclopropane-1-carboxylic acid (**V**) or its methyl ester **VI** that are precursors of conjugated dicyclopropanes. The hydrolysis of lactone **II** is accompanied by partial epimerization at the C^1 center to afford a mixture of (1*R*)- and (1*S*)-isomers **VI** and **VII** at a ratio of 4:1 (Scheme 2); the isomers can be separated by column chromatography on silica gel [5].

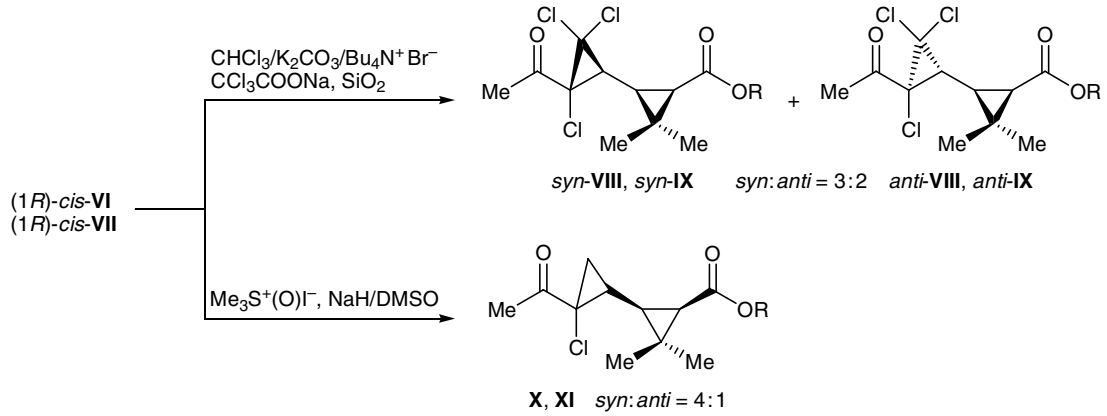
Cyclopropanation of the *Z*-configured double bond was performed with the (1*R*)-*cis* isomers of acid **V** esters, methyl ester **VI** and *m*-phenoxybenzyl ester **VII**. Dicyclopropanes **VIII**–**XI** were synthesized by the action of dichlorocarbene or sulfoxonium ylide on esters **VI** and **VII**. In both cases, we isolated mixtures of *syn* and *anti* diastereoisomers, the *syn* isomer prevailing, which is typical of cyclopropanation of *cis*-vinylcyclopropanes having an electron-deficient double bond [7]. The *syn*-to-*anti* ratio was 3:2 for compounds **VIII** and **IX** and 4:1 for **X** and **XI**. Diastereoisomeric esters **VIII** and **IX** were isolated as individual substances by column chromatography on silica gel.

Thus, from the transformation products of (+)-3-carene we obtained optically active dicyclopropanecarboxylic acid esters **VIII**–**XI** that can be regarded as analogs of highly efficient pyrethroids and fungicides; the products also attract interest as intermediate compounds in the synthesis of polycyclopropanes.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer at 300 and 75.46 MHz, respectively, from solutions in $CDCl_3$; the chemical shifts were measured relative to tetramethylsilane. The

Scheme 3.



VIII, **X**, R = Me; **IX**, **XI**, R = 3-$PhOC_6H_4CH_2$.

IR spectra were obtained in the frequency range from 400 to 4000 cm^{-1} on a Specord M-80 spectrometer from samples prepared as thin films. The optical rotations were measured from solutions in $CHCl_3$ on a Perkin–Elmer 241 MS instrument. GLC analysis was performed on a Chrom-5 chromatograph [1200×3-mm column, stationary phase 5% of SE-30 on Chromaton N-AW-DMSC (0.16–0.20 mm), oven temperature 50–300°C, carrier gas helium].

5,5-Dichloro-4,8,8-trimethyl-3-oxatricyclo-[5.1.0.0^{4,6}]octan-2-one (II). Compound **I**, 2 g (13.15 mmol), was dissolved in 50 ml of anhydrous chloroform, 0.315 g (0.98 mmol) of $Bu_4N^+Br^-$, 6 g (43.47 mmol) of K_2CO_3, 6.25 g (33.7 mmol) of CCl_3CO_2Na, and 0.1 ml of MeOH were added, and the mixture was heated for 4 h under reflux with stirring. The mixture was diluted with ethyl acetate, washed with water, and dried over Na_2SO_4, the solvent was distilled off, and the residue was subjected to chromatography on silica gel using petroleum ether–ethyl acetate (9:1) as eluent to isolate 1.66 g (83%) of compound **II** as a colorless crystalline substance which was identical to that described in [5].

5,5-Dibromo-4,8,8-trimethyl-3-oxatricyclo-[5.1.0.0^{4,6}]octan-2-one (III). Compound **I**, 2 g (13.15 mmol), was dissolved in 6 ml of anhydrous bromoform, 0.3 g (0.93 mmol) of $Bu_4N^+Br^-$, 5.4 g (39.13 mmol) of K_2CO_3, and 0.1 ml of MeOH were added, and the mixture was heated for 4 h under reflux with stirring. The mixture was diluted with ethyl acetate, washed with water, and dried over Na_2SO_4, the solvent was distilled off, excess bromoform was removed under reduced pressure, and the residue was subjected to chromatography on silica gel using petroleum ether–ethyl acetate (9:1) as eluent to isolate 1.7 g (85%) of compound **III** as a colorless crystalline substance which was identical to that described in [5].

Methyl 3,3-dimethyl-6-oxohept-4-enoate (IV). Compound **I**, 0.5 g (3.2 mmol), was dissolved in 6 ml of anhydrous methylene chloride, 0.03 g (0.098 mmol) of $Bu_4N^+Br^-$, 0.1 ml of MeOH, 3 ml of $CHCl_3$ or $CHBr_3$, and 0.52 g (13.1 mmol) of freshly calcined NaOH were added, and the mixture was heated for 6 h under reflux with stirring. The mixture was diluted with ethyl acetate, washed in succession with 3% hydrochloric acid and a saturated solution of NaCl, and dried over Na_2SO_4. The mixture was filtered, the solvent was distilled off from the filtrate, and the residue (0.58 g) was subjected to chromatography on silica gel using petroleum ether–ethyl acetate (19:1) as eluent to isolate 0.19 g (25%) of compound **II** and 0.39 g (65%) of **IV** or 0.2 g (19%) of **III** and 0.4 g (67%) of **IV**. The products were identical to those described in [5, 6].

Methyl 3-[(1*Z*)-2-chloro-3-oxobut-1-en-1-yl]-2,2-dimethylcyclopropane-1-carboxylate (VI). A mixture of 1 g (4.25 mmol) of compound **II**, 0.6 g of KOH, 0.6 ml of water, and 40 ml of MeOH was stirred for 6 h. The mixture was diluted with ethyl acetate, the organic phase was washed in succession with water and a saturated solution of NaCl, and dried over Na_2SO_4, and the solvent was distilled off. The residue (0.85 g) was subjected to column chromatography on silica gel using petroleum ether–ethyl acetate (19:1) to isolate 0.56 g (57%) of (1*R*)-*cis* isomer and 0.14 g (14%) of (1*S*)-*trans* isomer of **VI**, which were identical to those described in [5]. (1*S*)-*trans* Isomer: $[\alpha]_{589}^{20}$ = +71.9° (*c* = 0.17). ^{13}C NMR spectrum, δ_C, ppm: 20.15 and 26.19 (2-CH_3), 27.07 (C^2), 29.58 (C^1), 31.15 (**C**H_3CO), 36.47 (C^3), 51.93 (CH_3O), 133.78 (CCl), 138.48 (**C**=CCl), 171.25 (COO), 191.02 (C=O).

***m*-Phenoxybenzyl 3-[(1*Z*)-2-chloro-3-oxobut-1-en-1-yl)-2,2-dimethylcyclopropane-1-carboxylate (VII).** A mixture of 1.9 g (8.55 mmol) of compound **II**, 1.42 g (25.45 mmol) of KOH, 47 ml of H_2O, and 50 ml of MeOH was stirred for 6 h at 30–40°C. The mixture was poured into 9 ml of water and thoroughly washed with diethyl ether (2×30 ml), the aqueous phase was separated, acidified to pH 2 with dilute sulfuric acid, and extracted with diethyl ether (3×30 ml), the extracts were combined, washed with a saturated solution of NaCl, and dried over Na_2SO_4, and the solvent was distilled off. Yield of acid **V** 1.6 g (91%). IR spectrum, ν, cm^{-1}: 590 (C–Cl), 1630 (C=C), 1690 (C=O), 1720 (CO_2H), 2400–3400 (OH). Acid **V**, 0.3 g (1.3 mmol), was dissolved in 15 ml of anhydrous benzene, 0.2 ml of thionyl chloride was added dropwise under stirring, and the mixture was stirred at 70–80°C until gaseous products no longer evolved. The solvent was distilled off to leave 0.28 g of the corresponding acid chloride. IR spectrum, ν, cm^{-1}: 590 (C–Cl), 1630 (C=C), 1690 (C=O), 1780 (COCl).

A mixture of 0.614 g (3.07 mmol) of *m*-phenoxybenzyl alcohol, 5 ml of CH_2Cl_2, and 0.358 g (4.53 mmol) of pyridine was cooled to 10°C, 0.76 g (4 mmol) of acid **V** chloride was added, and the mixture was stirred for 4 h. Methylene chloride, 40 ml, and water, 10 ml, were added to the mixture at room temperature, the mixture was stirred for 30 min, the aqueous phase was separated, and the organic phase was washed in succession with 10% hydrochloric acid,

water, a solution of $NaHCO_3$, and a solution of NaCl and dried over Na_2SO_4. The solvent was distilled off, and the residue was subjected to column chromatography on silica gel using petroleum ether–ethyl acetate (19:1) as eluent to isolate 0.66 g (52%) of (1*R*)-*cis* and 0.165 g (13%) of (1*S*)-*trans* isomers of **VII**.

(1*R*)-*cis*-**VII**. $[\alpha]_{589}^{20} = -5.92°$ (c = 0.09). IR spectrum, ν, cm^{-1}: 590 (C–Cl), 1590 (C–C_{arom}), 1620 (C=C), 1690 (C=O), 1735 (COO). ^1H NMR spectrum, δ, ppm: 1.33 s (3H, 2-CH_3), 1.35 s (3H, 2-CH_3), 2.15 d (1H, 1-H, J = 8.5 Hz), 2.35 d.d (1H, 3-H, J = 8.5, 9.4 Hz), 2.42 s (3H, CH_3CO), 5.12 s (2H, CH_2), 6.92–7.41 m (9H, H_{arom}), 7.44 d (1H, CH=, J = 9.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 15.04, 25.88 (2-CH_3); 28.31 (C^1); 29.92 (C^2); 32.87 (**C**H_3CO); 34.05 (C^3); 65.88 (CH_2); 118.13, 118.36, 118.94, 119.23, 122.58, 123.42, 129.67, 129.83, 129.97 (C_{arom}); 134.68 (CCl); 137.96 (**C**=CCl); 138.24 (**C**CH_2); 156.75, 157.47 (C–O–C); 169.99 (COO); 190.89 (C=O).

(1*S*)-*trans*-**VII**. $[\alpha]_{589}^{20} = +7.204°$ (c = 0.04). IR spectrum, ν, cm^{-1}: 590 (C–Cl); 1600 (C–C_{arom}); 1625 (C=C); 1690 (C=O); 1735 (COO). ^1H NMR spectrum, δ, ppm: 1.23 s (3H, 2-CH_3), 1.35 s (3H, 2-CH_3), 1.92 d (1H, 1-H, J = 5 Hz), 2.40 s (3H, CH_3CO), 2.55 d.d (1H, 3-H, J = 5, 10 Hz), 5.13 s (2H, CH_2), 6.64 d (1H, CH=, J = 10 Hz), 6.92–7.42 m (9H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 20.26, 25.67 (2-CH_3); 26.52 (C^2); 31.05 (C^1); 31.44 (**C**H_3CO); 36.44 (C^3); 66.06 (CH_2); 118.19, 118.39, 118.77, 118.96, 122.64, 123.40, 129.71, 129.83, 130.05 (C_{arom}); 134.22 (CCl); 137.73 (**C**=CCl); 138.24 (**C**CH_2); 156.84, 157.47 (C–O–C); 170.21 (COO); 191.67 (C=O).

Methyl (1*R*)-*cis*-3-(2-acetyl-2,3,3-trichlorocyclopropyl)-2,2-dimethylcyclopropane-1-carboxylate (VIII). Compound **VI**, 0.5 g (2.2 mmol), was dissolved in 13 ml of anhydrous chloroform, 0.189 g (0.59 mmol) of $Bu_4N^+Br^-$, 2.4 g (17.4 mmol) of K_2CO_3, 4.25 g (22.9 mmol) of CCl_3CO_2Na, and 0.1 ml of MeOH were added, and the mixture was heated for 8 h under reflux with stirring. The mixture was diluted with ethyl acetate, washed with water, and dried over Na_2SO_4, the solvent was distilled off, and the residue (0.4 g) was subjected to column chromatography on silica gel using petroleum ether as eluent to isolate 0.24 g (35%) of *syn*-**VIII** and 0.16 g (23%) of *anti*-**VIII**. IR spectrum, ν, cm^{-1}: 560, 590 (C–Cl); 1600 (C–C_{arom}); 1720 (C=O); 1735 (COO).

syn-**VIII**. $[\alpha]_{589}^{20} = +1.4°$ (c = 0.1). ^1H NMR spectrum, δ, ppm: 1.18 t (1H, 3-H, $J_{3,1} = J_{3,1'}$ = 8.5 Hz), 1.22 s (3H, 2-CH_3), 1.27 s (3H, 2-CH_3), 1.76 d (1H, 1-H, J = 8.5 Hz), 2.54 s (3H, CH_3CO), 3.23 d (1H, 1′-H, J = 8.5 Hz), 3.73 s (3H, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: 14.95 (2-CH_3), 25.57 (C^2), 27.65 (2-CH_3), 28.12 (**C**H_3CO), 28.58 (C^1), 28.78 (C^3), 32.56 ($C^{1'}$), 51.74 (OCH_3), 59.60 ($C^{2'}$), 65.58 (CCl_2), 171.41 (COO), 195.83 (C=O).

anti-**VIII**. ^1H NMR spectrum, δ, ppm: 1.15 t (1H, 3-H, $J_{3,1} = J_{3,1'}$ = 8.6 Hz), 1.28 s (3H, 2-CH_3), 1.71 d (1H, 1-H, J = 8.6 Hz), 2.53 s (3H, CH_3CO), 3.32 d (1H, 1′-H, J = 8.6 Hz), 3.68 s (3H, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: 15.39 (2-CH_3), 25.47 (C^2), 27.95 (C^1), 28.08 (C^3), 28.27 (2-CH_3), 28.56 (**C**H_3CO), 32.95 ($C^{1'}$), 51.59 (OCH_3), 60.05 ($C^{2'}$), 65.85 (CCl_2), 171.13 (COO), 195.86 (C=O).

***m*-Phenoxybenzyl (1*R*)-*cis*-3-(2-acetyl-2,3,3-trichlorocyclopropyl)-2,2-dimethylcyclopropane-1-carboxylate (IX).** Compound (1*R*)-*cis*-**VII**, 0.2 g (0.484 mmol), was dissolved in 20 ml of anhydrous chloroform, 0.126 g (0.4 mmol) of $Bu_4N^+Br^-$, 0.89 g (6.5 mmol) of K_2CO_3, 0.95 g (5 mmol) of CCl_3CO_2Na, and 0.1 ml of MeOH were added, and the mixture was heated for 8 h under reflux with stirring. The mixture was diluted with ethyl acetate, washed with water, and dried over Na_2SO_4. The solvent was distilled off, and the residue was subjected to column chromatography on silica gel using petroleum ether–ethyl acetate (19:1) as eluent to isolate 0.08 g (33%) of *syn*-**IX** and 0.05 g (21%) of *anti*-**IX**. IR spectrum, ν, cm^{-1}: 560, 590 (C–Cl); 1600 (C–C_{arom}); 1720 (C=O); 1735 (COO).

syn-**IX**. $[\alpha]_{589}^{20} = -10.3°$ (c = 0.086). ^1H NMR spectrum, δ, ppm: 1.21 t (1H, 3-H, $J_{3,1} = J_{3,1'}$ = 8.5 Hz), 1.23 s (3H, 2-CH_3), 1.25 s (3H, 2-CH_3), 1.80 d (1H, 1-H, J = 8.5 Hz), 2.52 s (3H, CH_3CO), 3.26 d (1H, 1′-H, J = 8.5 Hz), 5.15 s (2H, CH_2), 6.91–7.40 m (9H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 14.36 (2-CH_3); 26.26 (C^2); 28.49 (2-CH_3); 29.85 (**C**H_3CO); 29.91 (C^1); 30.35 (C^3); 33.32 ($C^{1'}$); 60.61 ($C^{2'}$); 64.87 (CCl_2); 66.27 (CH_2); 118.53, 118.73, 119.39, 119.48, 123.05, 123.90, 130.19, 130.28, 130.52 (C_{arom}); 138.54 (**C**CH_2); 157.29, 157.95 (COC); 170.46 (COO); 195.50 (C=O).

anti-**IX**. ^1H NMR spectrum, δ, ppm: 1.17 t (1H, 3-H, $J_{3,1} = J_{3,1'}$ = 8.6 Hz), 1.26 s (3H, 2-CH_3), 1.29 s (3H, 2-CH_3), 1.76 d (1H, 1-H, J = 8.6 Hz), 2.39 s (3H, CH_3CO), 3.42 d (1H, 1′-H, J = 8.6 Hz), 5.17 s (2H, CH_2), 6.83–7.22 m (9H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 17.89 (2-CH_3); 24.52 (C^2); 27.44 (2-CH_3); 28.87 (**C**H_3CO); 29.03 (C^1); 29.54 (C^3); 32.85 ($C^{1'}$); 52.74 ($C^{2'}$); 60.24 (CCl_2); 65.38 (CH_2); 118.28, 118.91, 119.25, 119.53, 122.69, 122.72, 129.69, 129.75, 129.79

(C_{arom}); 137.97 (**C**CH_2); 156.86, 157.41 (COC); 170.58 (COO); 195.57 (C=O).

Methyl (1*R*)-*cis*-3-(2-acetyl-2-chlorocyclopropyl)-2,2-dimethylcyclopropane-1-carboxylate (X). Dimethyl sulfoxide, 1.5 ml, was slowly added under argon to a mixture of 0.29 g (1.32 mmol) of finely powdered trimethylsulfoxonium iodide and 0.032 g (2.6 mmol) of sodium hydride, and the mixture was stirred for 20 min at room temperature. The mixture was cooled to 10°C, a solution of 0.285 g (1.24 mmol) of (1*R*)-*cis*-**VI** in 0.7 ml of dimethyl sulfoxide was quickly added, and the mixture was stirred for 5 min at 10°C and for 2 h at room temperature, poured into 1.5 ml of ice water, and extracted with three portions of diethyl ether. The extracts were combined, washed with water and a saturated solution of NaCl, dried over Na_2SO_4, and evaporated. The residue was subjected to column chromatography on silica gel using petroleum ether as eluent to isolate 0.17 g (57%) of a mixture of *syn* and *anti* isomers of compound **X** at a ratio of 4:1. IR spectrum, ν, cm^{-1}: 590 (C–Cl), 1715 (C=O), 1735 (COO).

syn-**X**. ^{1}H NMR spectrum, δ, ppm: 1.05 t (1H, 3-H, J = 8.7 Hz), 1.17 d.d (1H, 3′-H_a, ^2J = 5.3, $J_{3',1'}$ = 8.2 Hz), 1.22 s (6H, 2-CH_3), 1.64 d (1H, 1-H, J = 8.7 Hz), 2.0 d.d (1H, 3′-H_b, ^2J = 5.3, $J_{3',1'}$ = 10.0 Hz), 2.27 d.d.d (1H, 1′-H, $J_{3',1'}$ = 10.0, 8.2, $J_{1',3}$ = 8.7 Hz), 2.42 s (3H, CH_3CO), 3.67 s (3H, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: 14.53 (2-CH_3), 25.62 (C^2), 26.63 (2-CH_3), 26.83 (CH_2), 27.62 (C^1), 28.22 (C^3), 28.72 (**C**H_3CO), 33.51 ($C^{1'}$), 51.88 (CH_3O), 52.44 ($C^{2'}$), 171.66 (COO), 204.08 (C=O).

anti-**X**. ^{1}H NMR spectrum, δ, ppm: 1.02 t (1H, 3-H, J = 8.5 Hz), 1.16 d.d (1H, 3′-H_b, ^2J = 5.2, $J_{3',1'}$ = 8.2 Hz), 1.30 s (6H, 2-CH_3), 1.68 d (1H, 1-H, J = 8.5 Hz), 1.89 d.d.d (1H, 1′-H, $J_{3',1'}$ = 9.9, 8.2, 8.5 Hz), 2.09 d.d (1H, 3′-H_a, ^2J = 5.2, $J_{3',1'}$ = 9.9 Hz), 2.37 s (3H, CH_3CO), 3.64 s (3H, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: 14.93 (2-CH_3), 25.63 (C^2), 25.82 (CH_2), 27.37 (2-CH_3), 27.46 (C^1), 28.16 (C^3), 29.60 (**C**H_3CO), 33.33 ($C^{1'}$), 51.33 ($C^{2'}$), 51.68 (CH_3O), 171.34 (COO), 205.13 (C=O).

***m*-Phenoxybenzyl (1*R*)-*cis*-3-(2-acetyl-2-chlorocyclopropyl)-2,2-dimethylcyclopropane-1-carboxylate (XI).** Dimethyl sulfoxide, 1.5 ml, was slowly added under argon to a mixture of 0.64 g (2.9 mmol) of finely powdered trimethylsulfoxonium iodide and 0.035 g (2.95 mmol) of sodium hydride, and the mixture was stirred for 20 min at room temperature. The mixture was cooled to 10°C, and a solution of 0.375 g (0.909 mmol) of (1*R*)-*cis*-**VII** in 0.7 ml of dimethyl sulfoxide was quickly added. The mixture was stirred for 5 min at 10°C and for 2 h at room temperature, poured into 1.5 ml of ice water, and extracted with diethyl ether. The extracts were combined, washed with water and a saturated solution of NaCl, dried over Na_2SO_4, and evaporated to isolate 0.26 g (67%) of a mixture of *syn* and *anti* isomers of **XI** at a ratio of 4:1. IR spectrum, ν, cm^{-1}: 580 (C–Cl), 1600 (C–C_{arom}), 1720 (C=O), 1735 (COO).

syn-**XI**. ^{1}H NMR spectrum, δ, ppm: 1.06 t (1H, 3-H, J = 8.7 Hz), 1.17 d.d (1H, 3′-H_a, ^2J = 5.3, $J_{3',1'}$ = 8.1 Hz), 1.23 s (6H, 2-CH_3), 1.71 d (1H, 1-H, J = 8.7 Hz), 1.98 d.d (1H, 3′-H_b, ^2J = 5.3, $J_{3',1'}$ = 10.1 Hz), 2.27 d.d.d (1H, 1′-H, $J_{1',3'}$ = 10.1, $J_{1',2'}$ = 8.1, $J_{1',3}$ = 8.7 Hz), 2.39 s (3H, CH_3CO), 5.06 s (2H, CH_2), 6.69–7.39 m (9H, H_{arom}).

anti-**XI**. ^{1}H NMR spectrum, δ, ppm: 1.05 t (1H, 3-H, J = 8.4 Hz), 1.16 d.d (1H, 3′-H_b, ^2J = 5.1, $J_{3',1'}$ = 8.1 Hz), 1.30 s (6H, 2-CH_3), 1.74 d (1H, 1-H, J = 8.4 Hz), 1.85 d.d.d (1H, 1′-H, $J_{1',3'}$ = 9.9, 8.1, $J_{1',3}$ = 8.4 Hz), 2.08 d.d (1H, 3′-H_a, ^2J = 5.1, $J_{3',1'}$ = 9.9 Hz), 2.43 s (3H, CH_3CO), 5.09 s (2H, CH_2), 6.69–7.39 m (9H, H_{arom}).

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