Organic Chemistry

Synthesis of enantiomeric *cis*-homocaronic acids from (+)-3-carene

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The syntheses of the dimethyl ester of (−)-(1*R*)-*cis*-homocaronic acid (7 steps, overall yield 43 %) and its antipode, the dimethyl ester of (+)-(1*S*)-*cis*-homocaronic acid (5 steps, overall yield 27 %), were performed starting from (+)-3-carene and its derivatives, (+)-4α-acetyl-2-carene and (+)-4α-acetoxymethyl-2-carene. Oxidative cleavage in the key stages was carried out by ozonization.

Key words: (+)-3-carene, dimethyl ester of (−)-(1*R*)-*cis*-homocaronic acid, dimethyl ester of (+)-(1*S*)-*cis*-homocaronic acid, synthesis, ozonolysis.

It is known that optically active pyrethroids are more effective than racemates for combating vermin.[1] The acid components of the optically active forms of pyrethroids are usually synthesized from natural (+)-3-carene (**1**) or its derivatives, (+)-4α-acetoxymethyl-2-carene (**2**) and (+)-4α-acetyl-2-carene (**3**)[2—4] obtained by relatively simple and efficient methods.[5]

In the present work we studied the synthesis of enanthiomeric methyl *cis*-2,2-dimethyl-3-(methoxycarbonylmethyl)cyclopropanecarboxylates **4** and **5**, esters of *cis*-homocaronic acids, from (+)-3-carene (**1**) and its derivatives **2** and **3**.

The dimethyl ester of (−)-(1*R*)-*cis*-homocaronic acid **4** was synthesized from (+)-3-carene **1** according to Scheme 1.

The most efficient method for the cleavage of (+)-3-carene **1** was found to involve ozonization in CH_2Cl_2 in the presence of Py to give ketoaldehyde (**6**)[6] in 95 % yield. The latter was transformed into ketoenol acetate (**7**) according to the known procedure.[6] Ozonization of compound **7** under the conditions indicated above gave ketoaldehyde (**8**) in 96 % yield, which is considerably higher than those reported previously.[6,7,8] Ketoaldehyde **8** was oxidized by the Jones reagent to give ketoacid (**9**) (59 %), which can also be obtained in a higher yield (63 %) directly from enol acetate **7** by ozonization in ethyl acetate followed by decomposition by the Jones reagent. The methyl ester (**10**) of ketoacid **9** was obtained by esterification of the latter (treatment with CH_2N_2 or MeI in DMSO in the presence of powdered KOH) in 95 % yield. Ketoester **10** reacts with Me_3SiCl in THF in the presence of lithium diisopropylamide (LDA) to give a silyl enol ether (**11**), whose structure was confirmed by IR, ^1H NMR, and mass spectral data

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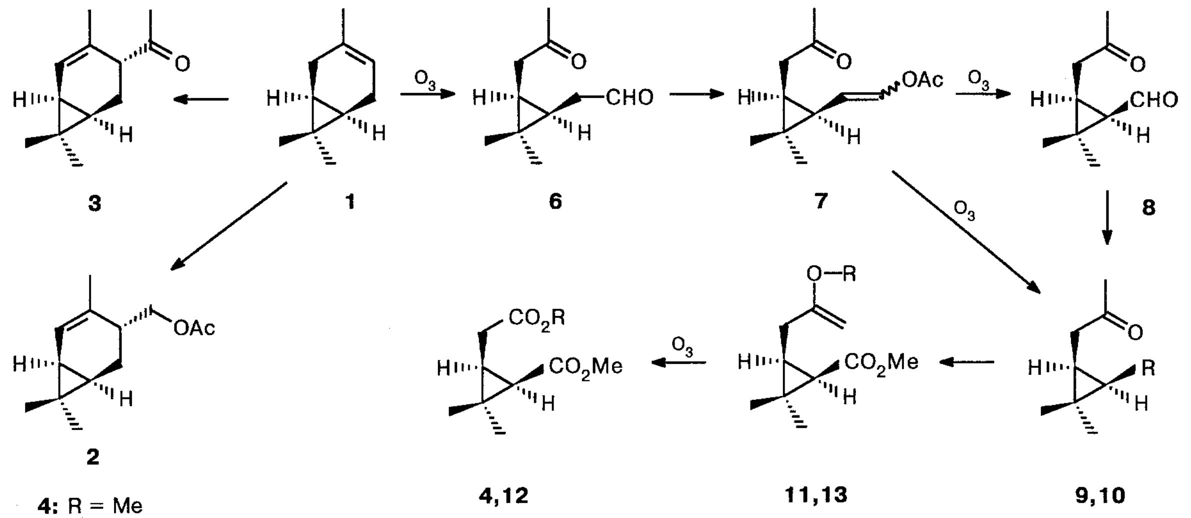
Scheme 1



4: R = Me
9: R = CO_2H
10: R = CO_2Me
11: R = Me_3Si
12: R = H
13: R = Ac

(see Experimental), in an almost quantitative yield (97 %). Ozonization of **11** in a mixture of dry MeOH and CH_2Cl_2 (2 : 1) followed by the decomposition of the ozonide with DMSO gave ester-acid (**12**), which was transformed into ester **4** by esterification with CH_2N_2. The structure of the product was confirmed by spectral data. The coupling constants of the protons at C(1) and C(3) (^3J = 8.4 Hz) imply their *cis*-orientation, in agreement with the data reported by other authors.[3,9,10] The yield of product **4** is 93 % with respect to the silyl enol ether **11**. It should be noted that the ozonization of the latter can also be successfully performed in a CH_2Cl_2—Py mixture, which simplifies the isolation of the product and decreases its yield (90 %) only slightly.

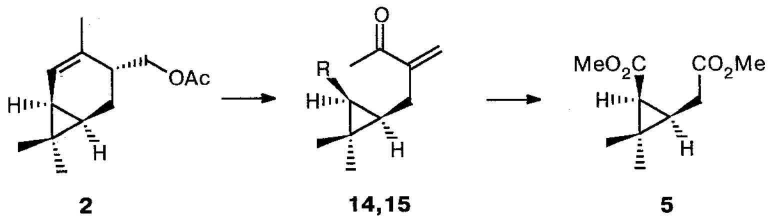
Contrary to our expectations, it turned out that treatment of ketoester **10** with Ac_2O in AcOEt in the presence of 70 % perchloric acid as the catalyst, *i.e.*, under the conditions of thermodynamic control of the reaction,[11,12] results in its transformation into enol acetate (**13**) (80 %) containing a terminal rather than an internal double bond. The presence of a vinyl group is confirmed by the IR (880, 1655 cm^{-1}) and ^1H NMR spectral data (a signal of two protons at 4.48—4.60 ppm). Ozonization of diester **13** in a CH_2Cl_2—Py mixture gives ester-acid **12** in 92 % yield.

As a result of the above transformations ester **4** was obtained from (+)-3-carene **1** in seven stages in 43 % overall yield.

We have previously found[13] that one of the ozonization products of acetate (+)-**2** is α,β-unsaturated ketoaldehyde (**14**) (Scheme 2).

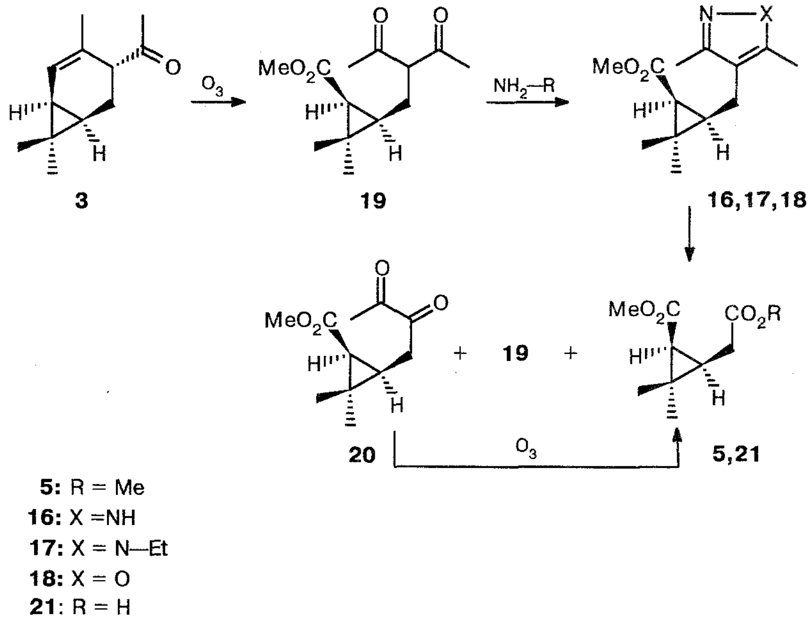
In the present work it was found that the complete ozonization of its dimethylacetal (**15**) in ethyl acetate at 0 °C followed by esterification with diazomethane results in the antipode of compound **4**, the dimethyl ester of (+)-(1*S*)-*cis*-homocaronic acid **5** in 56 % yield. The oxidation of an acetal group into an ester group during ozonolysis has been known previously.[14] The structure of diester **5** was confirmed by spectral data. Its constants

Scheme 2



14: R = CHO
15: R = $CH(OMe)_2$

Scheme 3



are in good agreement with those reported in the literature.[6,15–17]

Heterocyclic compounds readily obtained from the products of the transformation of (+)-4α-acetyl-2-carene **3** have been used by us previously as intermediates in the syntheses of the acid components of pyrethroids.[18,19] We thoroughly studied the ozonization of pyrazole (**16**), ethylpyrazole (**17**), and isoxazole (**18**) synthesized by the condensation of β-diketoester (**19**) with hydrazine hydrate, ethylhydrazine, and hydroxylamine, respectively.

Ozonization of pyrazole **16** resulted in a complex mixture of compounds. We managed to isolate and characterize two predominating components of the mixture. One of them is acidic and the other one is neutral. The latter component was identified as α-diketoester (**20**) based on elemental analysis, ^1H and ^{13}C NMR, IR, and UV spectral data.

The acid product (**21**) of the ozonization of pyrazole **16**, whose yield is small (5 %), undergoes methylation to give the dimethyl ester of (+)-(1*S*)-*cis*-homocaronic acid **5**.

The ozonolysis of ethylpyrazole **17** in MeOH followed by the reductive decomposition of the peroxides with DMSO occurs more clearly. Two main neutral products were found, namely, β-diketoester **19** (40 %) and α-diketoester **20** (40 %), which were identified by comparison with authentic samples. When ozonization was performed in CH_2Cl_2 in the presence of Py, the ratio of products **19**, **20**, and **5** changed insignificantly and their yields were 40, 30, and 10 %, respectively.

Ozonization of both unsubstituted pyrazole **16** and isoxazole **18** does not result in β-diketoester **19**. The reactions give α-diketoester **20** (58 %) and the monomethyl ester of (1*S*)-*cis*-homocaronic acid **21** (8 %), which undergoes esterification with CH_2N_2 yielding diester **5**.

Ozonization of α-diketoester **20** in AcOEt under the conditions described for dimethylacetal **15** gives a good yield (75 %) of ester-acid **21** identified as diester **5**.

Thus, (+)-4α-acetyl-2-carene **2** can be transformed into the dimethyl ester of (+)-(1*S*)-*cis*-homocaronic acid **5** *via* isoxazole **18** in five stages in 27 % overall yield.

Experimental

Specific rotation was measured on a Perkin-Elmer-141 polarimeter in $CHCl_3$. IR spectra were obtained on Specord-74-1 and UR-20 spectrophotometers, and UV spectra were recorded on a Shimadsu UV 365 spectrophotometer in EtOH. ^1H NMR spectra were recorded on Tesla BS-487 and BS-567 spectrometers, while ^{13}C NMR spectra were obtained on a Jeol FX-90 Q instrument (22.5 MHz) in $CDCl_3$ using $SiMe_4$ as the internal standard. Mass spectra were obtained on an MX-1320 spectrometer with a system for direct injection of compounds into the ion source, ionizing voltage 70 eV.

Treatment of solutions of the compounds in organic solvents included washing with water to neutral pH (in the case of acid solutions, washing with H_2O, 5 % KOH, and H_2O), drying with anhydrous $MgSO_4$ or Na_2SO_4, filtration, and removal of the solvent by distillation in the vacuum of a water-jet pump.

(+)-3-Carene (1), n_D^{20} = 1.4726, $[\alpha]_D^{20}$ +15.7° (in the pure form) (*cf.* Ref. 20: $[\alpha]_D^{25}$ +17.5° (in the pure form)).

(+)-4α-Acetoxymethyl-2-carene (2) (for the preparation method, see Ref. 4), n_D^{20} = 1.4765, $[\alpha]_D^{20}$ +132.0° (*c* 3.1) (*cf.* Ref. 4: n_D^{20} = 1.4756, $[\alpha]_D^{20}$ +133.6° (*c* 1.0)).

(+)-4α-Acetyl-2-carene (3) (for the preparation method, see Ref. 4), n_D^{20} = 1.4869, $[\alpha]_D^{20}$ +365.5° (in the pure form) (*cf.* Ref. 4: n_D^{20} = 1.4848, $[\alpha]^{20}$ +402°).

(+)-(1*R*,3*S*)-1-(2-Acetoxyvinyl)-2,2-dimethyl-3-(2-oxopropyl)cyclopropane (7) (for the preparation method, see Ref. 6), n_D^{20} = 1.4779, $[\alpha]_D^{20}$ +23.1 (*c* 3.0) (*cf.* Ref. 6: n_D^{14} = 1.4781).

(−)-(1*R*)-*cis*-2,2-Dimethyl-3-(2-oxopropyl)cyclopropylacetaldehyde (6). An ozone—oxygen mixture was passed with stirring through a solution of (+)-3-carene **1** (1.36 g, 10 mmol) in a mixture of dry CH_2Cl_2 (50 mL) and dry Py (2.5 mL) cooled to −78 °C until the ozone began to pass through the system. The solution was purged with a stream of nitrogen and heated to ~20 °C, then ether (150 mL) was added, and the solution was acidified with 5 % H_2SO_4. The organic layer was separated and worked-up in the usual way to give 1.59 g (95 %) of aldehyde **6** (pure according to TLC data). n_D^{20} = 1.4602, $[\alpha]_D^{20}$ − 4.0° (*c* 2.3) (*cf.* Ref. 6: n_D^{20} = 1.4601, $[\alpha]^{18}$ −4.1°).

(−)-(1*R*)-*cis*-2,2-Dimethyl-3-(2-oxopropyl)cyclopropanecarbaldehyde (8). Enol acetate **7** (2.1 g) was ozonized and the reaction mixture was worked-up as described above for (+)-3-carene **1**. The product (1.53 g) was chromatographed on a column with SiO_2 using hexane—ether (10 : 1) as the eluent to give 1.47 g (96 %) of compound **8** as a yellow liquid, n_D^{20} = 1.4658, $[\alpha]_D^{20}$ −2.17° (*c* 3.0) (*cf.* Ref. 8: n_D^{18} = 1.4660).

(−)-(1*R*)-*cis*-2,2-Dimethyl-3-(2-oxopropyl)cyclopropanecarboxylic acid (9). A. The Jones reagent obtained from CrO_3 (13.3 g), concentrated H_2SO_4 (11.5 mL), and H_2O (20 mL) was added dropwise at −15 °C to a stirred solution of aldehyde **8** (3.04 g, 19 mmol) in acetone (15 mL). The mixture was stirred for 1.5 h at the same temperature, and the excess reagent was neutralized with Pr^iOH. The mixture was diluted with water (50 mL) and extracted with ether (3×100 mL), washed with 5 % KOH, then with H_2O until a neutral medium was obtained, and worked-up in the usual way to give 1.3 g of a residue, which was not studied. The alkaline aqueous solution was acidified with 10 % H_2SO_4, extracted with ether (3×100 mL), and the combined extracts were worked-up in the usual way to give 1.98 g (59 %) of compound **9** as a colorless oil, $[\alpha]_D^{21}$ −2.71° (*c* 2.0). Found (%): C, 63.35; H, 28.08. $C_9H_{14}O_3$. Calculated (%): C, 63.51; H, 28.18. IR (CCl_4), ν/cm^{-1}: 1380, 1383 $(CMe)_2$, 1715 (C=O), 2560—3000 (CO_2H).

B. An ozone—oxygen mixture was passed with cooling (−10 °C) through a stirred solution of enol acetate **7** (2.1 g) in AcOEt (70 mL) until the reaction ceased. The solution was purged with a stream of nitrogen. Stirring was continued, and the Jones reagent (CrO_3, 1.04 g; H_2SO_4, 0.9 mL; H_2O, 3 mL) was added dropwise over a period of 20 min in such a way that the temperature did not exceed +5 °C. Stirring was continued for an additional 1 h, then H_2O (20 mL) was added, and the aqueous layer was separated and extracted with ether (3 × 50 mL). The extracts and the organic layer were combined, washed with brine (50 mL), and extracted with 10 % K_2CO_3 (4×50 mL). The alkaline solution was acidified with 10 % H_2SO_4, extracted with ether (3 × 100 mL), and worked-up in the usual way to give 1.05 g (63 %) of ketoacid **9**, which was identical with that described in procedure A.

Methyl (−)-(1*R*)-*cis*-2,2-dimethyl-3-(2-oxopropyl)cyclopropanecarboxylate (10). A. A solution of KOH (2.2 g, 39 mmol) in DMSO (20 mL) was stirred for 5 min, then ketoacid **9** (1.67 g, 9 mmol) and immediately MeI (2.37 g, 19 mmol) were added. The mixture was stirred for 15 min, poured into H_2O (200 mL), and extracted with CH_2Cl_2 (3×200 mL). The extract was worked-up in the usual way. The residue (1.72 g; 95 %) was ketoester **10**, a pale-yellow liquid, b.p. 55—58 °C (10.4 Torr), $[\alpha]_D^{22}$ −22.9° (*c* 1.6) (*cf.* Refs. 6,8: b.p. 57 °C at 0.3 Torr, $[\alpha]_D^{20}$ −23.7°.

B. Treatment of ketoacid **9** with an ethereal solution of CH_2N_2 gave ketoester **10** in a quantitative yield. Its spectroscopic characteristics were identical with those presented above (method **A**).

Methyl (+)-(1*R*)-*cis*-2,2-dimethyl-3-(2-trimethyloxopropyl-2-enyl)cyclopropanecarboxylate (11). Pr^i_2NH (5 g, 49 mmol) and a 2.45 *M* solution of *n*-butyllithium (20.6 mL) in hexane were added at −18 °C to dry THF (100 mL). The mixture was stirred for 10 min, cooled to −78 °C, and a solution of ketone **10** (8.28 g, 45 mmol) in THF (15 mL) was added dropwise. After 10 min, Me_3SiCl (12 mL, 94 mmol) was added with stirring, and the temperature was adjusted to ~20 °C. The mixture was stirred for an additional 2 h, poured into dry pentane, and filtered off. Evaporation of the solvent gave 12.8 g (97 %) of diester **11**, b.p. 90—95 °C/(0.2 Torr), $[\alpha]_D^{20}$ +1.65° (*c* 3.0, pentane). IR (CCl_4), ν/cm^{-1}: 1380, 1385 (CMe_2), 836 (C=CH_2), 1720 (CO_2Me). ^1H NMR, δ: 0.05—0.25 (m, 9 H, Me_3Si); 1.1 (s, 6 H, Me_2C); 1.31—1.55 (m, 1 H, HC(3)); 1.66—2.4 (m, 3 H, CH_2, HC(1)); 3.61 (s, 3 H, CO_2Me); 3.9—4.11 (m, 2 H, C=CH_2). MS, *m/z*: 256, 270, 250, 73 [Me_3Si], 75 [SiMeOH], 197 [M—CO_2Me], 225 $[M—OMe]_2$, 43.

Methyl (+)-(1*R*)-*cis*-2,2-dimethyl-3-(2-acetoxypropyl-2-enyl)cyclopropanecarboxylate (13). Ketoester **10** (0.33 g, 2 mmol) in dry AcOEt (1 mL) was added to a stirred mixture of Ac_2O (2.14 mL) and 70 % $HClO_4$ (0.035 mL) in dry AcOEt (13 mL). The mixture was stirred for 1 h at ~20 °C, and saturated aqueous $NaHCO_3$ was added until CO_2 was no longer evolved. The mixture was extracted with ether (3 × 50 mL), and the combined extract was worked-up in the usual way. The residue was chromatographed on SiO_2 using light petroleum ether—AcOEt (6 : 1) as the eluent to give 0.32 g (80 %) of compound **13** as a pale-yellow liquid, n_D^{20} = 1.4639, $[\alpha]_D^{20}$ +16.9 (*c* 1.06). Found (%): C, 63.57; H, 8.00; $C_{12}H_{18}O_4$. Calculated (%): C, 63.71; H, 8.01. IR (CCl_4), ν/cm^{-1}: 880, 1655 (C=CH_2), 1715 (COMe), 1735 (CO_2Me). ^1H NMR (CCl_4), δ: 0.86 (s), 1.05 (s, 6 H, Me_2C); 1.14 (d, 1 H, HC(1), *J* = 8.6 Hz); 2.00 (s, 3 H, $\underline{Me}CO$); 3.53 (s, 3 H, $\underline{Me}O_2C$); 4.48—4.60 (m, 2 H, C=CH_2).

Methyl (−)-(1*R*)-*cis*-2,2-dimethyl-3-(2-methoxycarbonylmethyl)cyclopropanecarboxylate (4). A. An ozone—oxygen mixture was passed at −78 °C through a solution of siloxyester **11** (8.8 g, 30 mmol) in a mixture of dry MeOH (100 mL) with CH_2Cl_2 (50 mL) until the solution became permanently blue. The mixture was purged with a stream of nitrogen, and Me_2S (9.6 mL) was added. The mixture was stirred for 2 h at the same temperature and left overnight at ~20 °C. The solution was diluted with ether (200 mL), and the organic layer was washed with brine and 5 % KOH (3 × 50 mL). The combined aqueous extract was acidified with cooling (3—5 °C) with 10 % H_2SO_4 and extracted with ether (3 × 50 mL). The ethereal extract was worked-up in the usual way, and an ethereal solution of CH_2N_2 was added to the residue of compound **12** (5.19 g) to give 5.58 g (93 %) of diester **4**, b.p. 108—113 °C/(13 Torr), n_D^{22} = 1.4473, $[\alpha]_D^{20}$ −28.0° (*c* 1.3). Found (%): C, 59.90; H, 7.87. $C_{10}H_{16}O_4$. Calculated (%): C, 59.86; H, 8.04. IR (CCl_4), ν/cm^{-1}: 1380, 1385, (Me_2C); 1720, 1745 (CO_2Me). ^1H NMR, δ: 1.18 (s); 1.20 (s, 6 H, Me_2C); 1.43 (d+t, 2 H, 1 H, HC(3), *J* = 6.9 Hz); 1.55 (d, 1 H, HC(1), *J* = 8.4 Hz); 2.76 (d, 2 H, CH_2, *J* = 6.9 Hz); 3.63 (s); 3.67 (s, 6 H, 2CO_2Me). ^{13}C NMR, δ: 173.57 (s); 172.07 (s, 2CO_2); 51.57 (q,); 51.17 (q, 2 $CO_2\underline{Me}$); 28.53 (t, CH_2); 28.53 (q, MeC); 28.13 (d, HC(1), HC(3));

25.38 (s, Me_2C); 14.17 (q, MeC). MS, *m/z* (I_{rel}(%)): 200, 185 [M—Me], 168 [M—MeOH], 169 [M—OMe]; 141 [M—CO_2Me], 140 [M—HCO_2Me], 136 [M—2MeOH], 109, 99, 95, 59 [CO_2Me].

B. Diester **13** (0.32 g) was ozonized and worked-up as described above for (+)-3-carene **3**. Treatment of the resulting product **12** (0.24 g) with an ethereal solution of CH_2N_2 gave 0.26 g (92 %) of diester **4** identical to that described above (method **A**).

Methyl (+)-(1*S*)-*cis*-2,2-dimethyl-3-(2,3-dioxobutyl)cyclopropanecarboxylate (20). A. An ozone—oxygen mixture was passed with stirring and cooling (−50 °C) through a solution of ethylpyrazole **17** (2 g, 7 mmol) in MeOH (30 mL) until the reaction ceased. The mixture was purged with a stream of nitrogen, Me_2S (3.2 mL) was added, and the mixture was stirred for 2 h at the same temperature and left overnight at ~20 °C. The mixture was diluted with ether (100 mL) and washed with brine and 5 % KOH. The residue (2 g) was worked-up in the usual way and chromatographed on SiO_2 (using hexane—EtOAc (10 : 1) as the eluent) to give 0.64 g (40 %) of product **20** as a yellow liquid, n_D^{20} = 1.4640, $[\alpha]_D^{20}$ +23.06° (*c* 3.0). Found (%): C, 63.13; H, 7.47. $C_{11}H_{16}O_4$. Calculated (%): C, 63.26; H, 7.59. IR (CCl_4), ν/cm^{-1}: 1720 (—CO—CO—), 1735 (CO_2Me). ^1H NMR, δ: 1.15 (s); 1.23 (s, 6 H, Me_2C); 1.25—1.49 (m, 1 H, HC(3)); 1.62 (d, 1 H, HC(1), *J* = 8 Hz); 2.31 (s, 3 H, MeCO); 3.11—3.28 (m, 2 H, CH_2); 3.64 (s, 3 H, CO_2Me). ^{13}C NMR, δ: 200.95 (s, $Me\underline{C}O$); 198.37 (s, CH_2CO); 171.96 (s, CO_2); 51.16 (q, $CO_2\underline{Me}$); 31.40 (t, CH_2); 28.66 (q,); 15.36 (q, $\underline{C}Me_2$); 20.93 (d, HC(3)); 28.46 (q, $\underline{Me}CO$). UV, λ_{max}/nm (ε): 280 (6920).

B. Ozonization of isoxazolylester **18** (1.5 g) in a mixture of CH_2Cl_2 (150 mL) and Py (7.5 mL) by a procedure similar to that used for (+)-3-carene **3** gave 0.77 g (58 %) of compound **20**, whose spectroscopic characteristics were identical with those presented above (**A**), and 92 mg (8 %) of acid **21**.

C. Ozonization of pyrazole **16** (1 g) in MeOH (15 mL) followed by reduction of the peroxide oxidation products by a procedure similar to that described above (**A**) gave 80 mg (10 %) of α-diketoester **20** and 0.23 g (35 %) of acid **21**.

Methyl (+)-(1*S*)-*cis*-2,2-dimethyl-3-(methoxycarbonylmethyl)cyclopropanecarboxylate (5). A. Dimethylacetal[10] **15** (4 g, 17 mmol) in AcOEt was ozonized at 0 °C, additionally oxidized for 5 h with oxygen, and purged with nitrogen. Me_2S (4 mL) was added, and the mixture was left overnight. The solvent was removed, and the resulting mixture (4.3 g) was treated with an ethereal solution of CH_2N_2. Conventional work-up gave 4.5 g of a residue, which was chromatographed on SiO_2 using hexane—ether (10 : 1) as the eluent to give 2.0 g (56.6 %) of diester **5**, n_D^{16} = 1.4580, $[\alpha]_D^{26}$ +25.8° (*c* 2.75). The spectroscopic characteristics of the product were identical with those of enantiomer **4**.

B. Ozonization of α-diketoester **20** (0.64 g, 3 mmol) in AcOEt (10 mL) followed by reduction of peroxide products with Me_2S (1.0 mL) similarly to method **A** gave 0.42 g (76 %) of diester **5** (*cf.* Refs. 6 and 4, respectively: $[\alpha]_D^{20}$ +37.5°, $[\alpha]_D^{20}$ +42.8°).

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