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Synthesis of Highly Functionalized Cyclobutene Derivatives

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Summary. Protonation of the reactive 1:1 intermediates produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates with CH-acids, such as ethyl 2,4-dioxo-hexanoate and ethyl 2,4-dioxo-5-methylhexanoate, lead to vinyltriphenylphosphonium salts, which undergo an intramolecular *Wittig* reaction to produce cyclobutene derivatives in fairly high yields.

Keywords. Cyclobutene derivatives; CH-acid; Intramolecular *Wittig* reaction; Acetylenic esters.

Introduction

Although several strategies for the synthesis of cyclobutenes have been developed in the past [1–3], this class of cyclenes is generally not easily accessible. In recent years, several routes to cyclobutenes *via* cycloaddition reactions have been described [4–6]. However, the general applicability of these methods is limited. We previously have described the synthesis of cyclobutene derivatives from the stereoselective intramolecular *Wittig* reaction of a vinyltriphenylphosphonium salt [7–9]. As part of our current studies on the development of new routes to heterocyclic and carbocyclic systems, we now report a covenient and facile synthesis of functionalized cyclobutene derivatives *via* intramolecular *Wittig* reaction.

Results and Discussion

The reactions of triphenylphosphine and dialkyl acetylenedicarboxylates **1** in the presence of a strong CH-acid, such as ethyl 2,4-dioxopentanoate (**2a**), lead to diastereomeric cyclobutene isomers **3** in high yields (Scheme 1).

We have not yet established a mechanism for the formation of **3** in an experimental manner, but a possible explanation is proposed in Scheme 2. On the basis of the well-established chemistry of trivalent phosphorus nucleophiles [10–14], it is reasonable to assume that **3** results from initial addition of triphenylphosphine to

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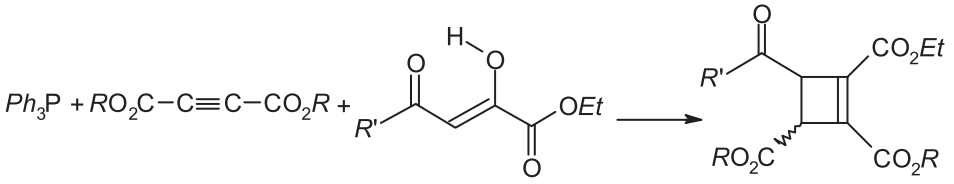
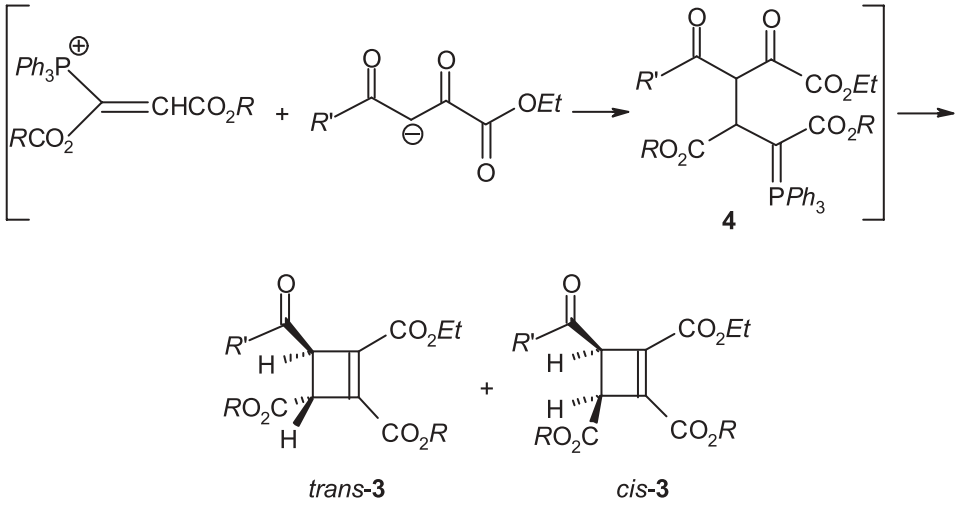


R	R'	R	R'
1a *Me*	**2a** *Me*	**3a** *Me*	*Me*
1b *Et*	**2b** *Et*	**3b** *Et*	*Me*
1c *t-Bu*	**2c** *i-Pr*	**3c** *t-Bu*	*Me*
		3d *Me*	*Et*
		3e *Et*	*Et*
		3f *t-Bu*	*Et*
		3g *Me*	*i-Pr*
		3h *Et*	*i-Pr*
		3i *t-Bu*	*i-Pr*

Scheme 1



Scheme 2

the acetylenic ester and subsequent protonation of the 1:1 adduct by **2**. Then, the positively charged ion might be attacked by the conjugate base of the CH-acid to form the phosphorane **4**, which is converted to **3** under the reaction conditions employed.

Compounds **3** possess two stereogenic centers, and two diastereoisomers are expected. In fact, the NMR spectra of **3a**–**3i** show the presence of both isomers. The $^{3}J_{HH}$ values of the two adjacent methine groups have been employed to assign the relative configuration.

The structures of **3a**–**3i** were deduced from their elemental analyses and their IR, ^{1}H, and ^{13}C NMR spectra. The ^{1}H NMR spectra of the cyclobutene derivatives display signals at about $\delta = 3.80$–4.02 ppm for the two methine groups (doublets, $^{3}J_{HH} = 3.0$–6.0 Hz), in agreement with the *cis* geometry of these protons together

with signals at about $\delta = 3.55–4.12$ ppm for the two methine groups (doublets, $^3J_{HH} = 0.5–2.0$ Hz) in agreement with a *trans* arrangement of these protons [15]. The ^{13}C NMR spectra of cyclobutene derivatives **3a–3i** exhibit two signals at about $\delta = 44–46$ and 44–52 ppm for the two CH groups of *cis* and *trans* isomers. A partial assignment of ^{13}C signals of **3a–3i** is given in the Experimental. The results show that bulky substituents prefere the *trans* geometry of **3**. Diastereomeric ratios were determined by ^1H NMR spectroscopy.

In conclusion, we have developed an efficient synthesis of highly functionalized cyclobutene derivatives. The method carries the advantage of being performed under neutral conditions and requires no activation or modification of the educts. The procedure is simple, the reaction conditions are mild, and the yields are fairly good.

Experimental

Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. These results agreed favorably with the calculated values. IR spectra were measured on a Shimadzu IR 460 spectrometer. ^1H and ^{13}C NMR spectra ($CDCl_3$) were measured on a Bruker DRX-500 Avance spectrometer. The mass spectra were recorded on a Shimadzu QP-1100-EX GC-Mass spectrometer operating at an ionization potential of 70 eV. Dialkyl acetylenedicarboxylates **1** and triphenylphosphine were obtained from Fluka (Buchs, Switzerland) and used without further purification.

Preparation of Ethyl 2,4-dioxoalkanoates **2** (See Ref. [16])

Compounds **2** were prepared from 10 mmol of diethyl oxalate and 10 mmol of aliphatic ketones in the presence of 10 mmol of sodium ethoxide using 30 cm^3 of ethanol as the solvent.

Ethyl 2,4-dioxopentanoate (**2a**, $C_7H_{10}O_4$)

Colorless liquid, bp 130–135°C/35 mm Hg (Ref. [17] 130°C/37 mm Hg), yield 1.26 g (79%); IR (KBr): $\bar{\nu} = 1729$ (C=O), 1628 and 1592 (C=C) cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): $\delta = 1.42$ (t, $J = 7.0$ Hz, CH_3), 2.28 (s, CH_3CO), 4.38 (q, $J = 7.0$ Hz, OCH_2), 6.40 (s, C=C–H), 13.66 (br s, OH) ppm; ^{13}C NMR (22.5 MHz, $CDCl_3$): $\delta = 13.31$ (CH_3), 26.79 (CH_3CO), 61.81 (OCH_2), 101.51 (=C–H), 161.37 (C=O ester), 166.46 (=C–OH), 199.65 (C=O) ppm.

Ethyl 2,4-dioxohexanoate (**2b**, $C_8H_{12}O_4$)

Colorless liquid, bp 145–150°C/35 mm Hg, yield 0.99 g (57%); IR (KBr): $\bar{\nu} = 1728$ (C=O), 1631 and 1591 (C=C) cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): $\delta = 1.16$ and 1.36 (2t, $J = 6.5$ Hz, $2CH_3$), 2.62 (q, $J = 6.5$ Hz, CH_2CO), 4.34 (q, $J = 6.5$ Hz, OCH_2), 6.42 (s, C=C–H), 14.07 (br s, OH) ppm; ^{13}C NMR (22.4 MHz, $CDCl_3$): $\delta = 8.26$ and 13.70 ($2CH_3$), 33.84 (CH_2CO), 62.18 (OCH_2), 101.02 (C=*C*–H), 161.90 (C=O ester), 165.93 (C=*C*–OH), 203.84 (C=O) ppm.

Ethyl 5-methyl-2,4-dioxohexanoate (**2c**, $C_9H_{14}O_4$)

Colorless liquid, bp 150–154°C/30 mm Hg, yield 1.31 g (70%); IR (KBr): $\bar{\nu} = 1728$ (C=O), 1634 and 1592 (C=C) cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): $\delta = 1.22$ (d, $J = 6.5$ Hz, CH*Me*$_2$), 1.42 (t, $J = 6.5$ Hz, CH_3), 2.72 (sept, $J = 6.5$ Hz, C*H*Me$_2$), 4.42 (q, $J = 6.5$ Hz, OCH_2), 6.46 (s, C=C–H), 14.01 (br s, OH) ppm; ^{13}C NMR (22.4 MHz, $CDCl_3$): $\delta = 13.56$ (CH_3), 18.12 (CH*Me*$_2$), 38.56 (C*H*Me$_2$), 61.97 (OCH_2), 99.60 (C=*C*–H), 161.70 (C=O ester), 166.79 (C=*C*–OH), 206.74 (C=O) ppm.

General Procedure for the Synthesis of **3** (Examplified by **3a**)

To a magnetically stirred solution of 0.524 g of triphenylphosphine (1 mmol) and 0.316 g of ethyl 2,4-dioxopentanoate **2a** (1 mmol) in 20 cm^3 of CH_2Cl_2 a mixture of 0.284 g of dimethyl acetylenedicarboxylate (1 mmol) in 2 cm^3 of CH_2Cl_2 was added dropwise at $-5°C$ over 10 min. The reaction mixture was then allowed to warm to room temperature and stirred for 24 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (Merck silica gel 60, 70–230 mesh) using *n*-hexane:ethyl acetate = 8:2 as eluent. The solvent was removed to afford **3a** as a pale yellow oil. The ^1H NMR spectrum of the crude product was consistent with a mixture of *cis*:*trans* isomers = 9:1.

Dimethyl 4-acetyl-1-(ethoxycarbonyl)cyclobut-1-ene-2,3-dicarboxylate (**3a**, $C_{13}H_{16}O_7$)

Pale yellow oil, yield 0.51 g (90%); IR (KBr): $\bar{\nu} = 1730$ and 1696 (C=O), 1635 (C=C) cm^{-1}; MS: m/z (%) = 285 ($M^+ + 1$, 8), 254 (25), 211 (12), 181 (36), 122 (19), 59 (100).

Major isomer (*cis*-**3a**) (90%); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.36$ (t, $J = 7.0$ Hz, CH_3), 2.60 (s, CH_3CO), 3.69 and 3.72 (2s, $2OCH_3$), 4.01 (d, $J = 5.5$ Hz, CH), 4.03 (d, $J = 5.5$ Hz, CH), 4.26–4.36 (m, OCH_2) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 14.03$ (CH_3), 29.39 (CH_3CO), 44.65 and 44.66 (2CH), 52.47 and 52.49 ($2OCH_3$), 61.69 (OCH_2), 137.05 and 148.01 (C=C), 159.93, 168.83, and 168.88 (3C=O ester), 193.65 (C=O) ppm.

Minor isomer (*trans*-**3a**) (10%); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.25$ (t, $J = 7.0$ Hz, CH_3), 2.34 (s, CH_3CO), 3.82 and 3.86 (2s, $2OCH_3$), 3.97 (d, $J = 1.6$ Hz, CH), 4.02 (d, $J = 1.6$ Hz, CH), 4.10–4.30 (m, OCH_2) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 14.02$ (CH_3), 29.45 (CH_3CO), 45.14 and 52.33 (2CH), 52.41 and 52.81 ($2OCH_3$), 61.56 (OCH_2), 140.77 and 142.60 (C=C), 159.86, 160.04, and 169.58 (3C=O ester), 202.86 (C=O) ppm.

Triethyl 4-acetylcyclobut-1-ene-1,2,3-tricarboxylate (**3b**, $C_{15}H_{20}O_7$)

Pale green oil, yield 0.58 g (93%); IR (KBr): $\bar{\nu} = 1725$ and 1705 (C=O), 1645 (C=C) cm^{-1}; MS: m/z (%) = 313 ($M^+ + 1$, 10), 268 (60), 222 (35), 236 (78), 195 (100), 167 (68).

Major isomer (*cis*-**3b**) (60%); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.23$–1.36 (3t, $J = 7.0$ Hz, $3CH_3$), 2.60 (s, CH_3CO), 3.99 (d, $J = 5.6$ Hz, CH), 4.01 (d, $J = 5.6$ Hz, CH), 4.10–4.34 (m, $3OCH_2$) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 14.04$, 14.07, and 14.12 ($3CH_3$), 29.32 (CH_3CO), 44.77 and 45.00 (2CH), 61.40, 61.62, and 61.63 ($3OCH_2$), 137.13 and 148.20 (C=C), 160.05, 168.35, and 168.39 (3C=O ester), 193.66 (C=O) ppm.

Minor isomer (*trans*-**3b**) (40%); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.30$–1.36 (3t, $J = 7.0$ Hz, $3CH_3$), 2.34 (s, CH_3CO), 3.82 (d, $J = 1.9$ Hz, CH), 3.98 (d, $J = 1.9$ Hz, CH), 4.20–4.30 (m, $3OCH_2$) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 14.10$, 14.11, and 14.12 ($3CH_3$), 29.32 (CH_3CO), 44.77 and 53.09 (2CH), 61.40, 61.42, and 61.62 ($3OCH_2$), 141.32 and 142.16 (C=C), 159.69, 160.02, and 169.14 (3C=O ester), 203.01 (C=O) ppm.

Di-tert-butyl 4-acetyl-1-(ethoxycarbonyl)cyclobut-1-ene-2,3-dicarboxylate (**3c**, $C_{19}H_{28}O_7$)

Pale yellow oil, yield 0.68 g (92%); IR (KBr): $\bar{\nu} = 1722$ and 1696 (C=O), 1640 (C=C) cm^{-1}; MS: m/z (%) = 368 (M^+, 4), 312 (42), 268 (100), 222 (57), 194 (60), 121 (29).

Major isomer (*trans*-**3c**) (80%); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.34$ (t, $J = 7.0$ Hz, CH_3), 1.47 and 1.51 (2s, $2OCMe_3$), 2.32 (s, CH_3CO), 3.68 (d, $J = 1.5$ Hz, CH), 3.89 (d, $J = 1.5$ Hz, CH), 4.27 (q, $J = 7.1$ Hz, OCH_2) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 14.14$ (CH_3), 27.95 and 27.80 ($2OCMe_3$), 31.00 (CH_3CO), 46.36 and 52.18 (2CH), 61.52 (OCH_2), 82.32 and 82.71 ($2OCMe_3$), 140.41 and 143.38 (C=C), 158.94, 160.27, and 168.38 (3C=O ester), 203.91 (C=O) ppm.

Minor isomer (*cis*-**3c**) (20%); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.10$ (t, $J = 7.0$ Hz, CH_3), 1.43 and 1.44 (2s, $2OCMe_3$), 2.27 (s, CH_3CO), 3.88 (d, $J = 5.5$ Hz, CH), 4.00 (d, $J = 5.5$ Hz, CH), 4.21 (q, $J = 7.1$ Hz, OCH_2) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 13.95$ (CH_3), 27.72 and 27.98 ($2OCMe_3$), 30.41 (CH_3CO), 45.60 and 45.86 (2CH), 62.20 (OCH_2), 81.90 and 82.70 ($2OCMe_3$), 136.62 and 148.50 (C=C), 159.06, 167.66, and 167.90 (3C=O ester), 196.02 (C=O) ppm.

Dimethyl 4-propionyl-1-(ethoxycarbonyl)cyclobut-1-ene-2,3-dicarboxylate (**3d**, $C_{14}H_{18}O_7$)

Pale yellow oil, yield 0.58 g (97%); IR (KBr): $\bar{\nu} = 1730$ and 1710 (C=O), 1638 (C=C) cm^{-1}; MS: m/z (%) = 298 (M^+, 15), 253 (100), 222 (23), 137 (54), 151 (37), 137 (60), 59 (78).

Major isomer (*cis*-**3d**) (90%); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.12$ and 1.32 (2t, $J = 7.0$ Hz, $2CH_3$), 2.97–3.04 (m, CH_2CO), 3.72 and 3.76 (2s, $2OCH_3$), 4.01 (d, $J = 5.5$ Hz, CH), 4.04 (d, $J = 5.5$ Hz, CH), 4.26–4.30 (m, OCH_2) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 7.20$ and 13.90 ($2CH_3$), 34.96 (CH_2CO), 44.58 and 44.76 (2CH), 52.18 and 52.53 ($2OCH_3$), 61.53 (OCH_2), 136.30 and 148.17 (C=C), 159.94, 168.84, and 168.91 (3C=O ester), 196.83 (C=O) ppm.

Minor isomer (*trans*-**3d**) (10%); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.09$ and 1.43 (2t, $J = 7.1$ Hz, $2CH_3$), 2.66–2.72 (m, CH_2CO), 3.74 and 3.82 (2s, $2OCH_3$), 3.71 (d, $J = 1.02$ Hz, CH), 3.98 (d, $J = 1.02$ Hz, CH), 4.70–4.80 (m, OCH_2) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 7.33$ and 13.94 ($2CH_3$), 35.04 (CH_2CO), 44.60 and 51.14 (2CH), 52.34 and 52.49 ($2OCH_3$), 61.54 (OCH_2) 140.61 and 142.70 (C=C), 159.71, 159.98, and 169.75 (3C=O ester), 205.59 (C=O) ppm.

Triethyl 4-propionylcyclobut-1-ene-1,2,3-tricarboxylate (**3e**, $C_{16}H_{22}O_7$)

Pale yellow oil, yield 0.60 g (92%); IR (KBr): $\bar{\nu} = 1728$ and 1705 (C=O), 1649 (C=C) cm^{-1}; MS: m/z (%) = 326 (M^+, 6), 280 (100), 297 (58), 235 (35), 135 (56), 73 (70).

Major isomer (*cis*-**3e**) (60%); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.13$ (t, $J = 7.2$ Hz, CH_3), 1.20–1.41 (m, $3CH_3$), 2.99–3.06 (m, ABX_3 system, CH_2CO), 3.98 (d, $J = 5.5$ Hz, CH), 4.02 (d, $J = 5.5$ Hz, CH), 4.12–4.31 (m, $3OCH_2$) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 7.36$, 14.05, 14.07, and 14.11 ($4CH_3$), 35.17 (CH_2CO), 44.82 and 45.04 (2CH), 61.42, 61.44, and 61.61 ($3OCH_2$), 136.31 and 148.37 (C=C), 160.13, 168.39, and 168.50 (3C=O ester), 197.14 (C=O) ppm.

Minor isomer (*trans*-**3e**) (40%); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.09$ (t, $J = 7.2$ Hz, CH_3), 1.20–1.41 (m, $3CH_3$), 2.59–2.74 (m, ABX_3 system, CH_2CO), 3.74 (d, $J = 1.6$ Hz, CH), 3.97 (d, $J = 1.6$ Hz, CH), 4.12–4.31 (m, $3OCH_2$) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 7.44$, 14.07, 14.09, and 14.11 ($4CH_3$), 35.79 (CH_2CO), 45.15 and 52.08 (2CH), 61.43, 61.55, and 61.62 ($3OCH_2$), 141.32 and 142.28 (C=C), 159.69, 160.69, and 169.25 (3C=O ester), 205.87 (C=O) ppm.

Di-tert-butyl 4-propionyl-1-(ethoxycarbonyl)cyclobut-1-ene-2,3-dicarboxylate (**3f**, $C_{20}H_{30}O_7$)

Pale green oil, yield: 0.70 g (91%); IR (KBr): $\bar{\nu} = 1728$ and 1696 (C=O), 1542 (C=C) cm^{-1}; MS: m/z (%) = 382 (M^+, 5), 337 (85), 282 (100), 208 (65), 135 (45), 106 (38).

Major isomer (*trans*-**3f**) (90%); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.06$ and 1.30 (2t, $J = 7.0$ Hz, $2CH_3$), 1.47 and 1.51 (2s, $2OCMe_3$), 2.59–2.74 (m, ABX_3 system, CH_2CO), 3.65 (s, CH), 3.89 (s, CH), 4.26 (q, $J = 7.1$ Hz, OCH_2) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 7.47$ and 14.17 ($2CH_3$), 27.95 and 27.98 ($2CMe_3$), 35.59 (CH_2CO), 46.49 and 51.79 (2CH), 61.37 (OCH_2), 82.08 and 82.48 ($2OCMe_3$), 140.57 and 143.29 (C=C), 158.99, 160.24, and 168.39 (3C=O ester), 206.38 (C=O) ppm.

Minor isomer (*cis*-**3f**) (10%); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.12$ and 1.33 (2t, $J = 7.0$ Hz, $2CH_3$), 1.43 and 1.47 (2s, $2OCMe_3$), 2.94–3.07 (m, ABX_3 system, CH_2CO), 3.83 (d, $J = 5.3$ Hz, CH), 3.89 (d, $J = 5.3$ Hz, CH), 4.28 (q, $J = 7.2$ Hz, OCH_2) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 7.30$ and 14.17 ($2CH_3$), 27.95 and 27.96 ($2OCMe_3$), 35.10 (CH_2CO), 46.64 and 45.87 (2CH),

61.32 (OCH_2), 81.94 and 82.01 ($2OCMe_3$), 136.30 and 148.86 (C=C), 160.32, 167.68, and 167.96 (3C=O ester), 197.41 (C=O) ppm.

Dimethyl 4-isobutyryl-1-(ethoxycarbonyl)cyclobut-1-ene-2,3-dicarboxylate (**3g**, $C_{15}H_{20}O_7$)

Pale yellow oil, yield 0.60 g (96%); IR (KBr): $\bar{\nu}$ = 1728 and 1700 (C=O), 1670 (C=C) cm^{-1}; MS: m/z (%) = 313 (M^+, 14), 226 (100), 208 (85), 166 (20), 139 (35), 80 (19).

Major isomer (*cis*-**3g**) (80%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.15 and 1.16 (2d, J = 7.0 Hz, CH*Me*$_2$), 1.32 (t, J = 7.0 Hz, CH_3), 3.60 (sept, J = 7.0 Hz, C*H*Me$_2$), 3.72 and 3.76 (2s, $2OCH_3$), 4.02 (d, J = 5.5 Hz, CH), 4.07 (d, J = 5.5 Hz, CH), 4.24–4.34 (m, OCH_2) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 14.04 (CH_3), 17.34 and 18.57 (CH*Me*$_2$), 38.80 (*C*HMe$_2$), 44.74 and 45.03 (2CH), 52.42 and 52.60 ($2OCH_3$), 61.57 (OCH_2), 136.13 and 148.23 (C=C), 159.74, 168.26, and 168.87 (3C=O ester), 199.72 (C=O) ppm.

Minor isomer (*trans*-**3g**) (20%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.12 and 1.22 (2d, J = 7.0 Hz, CH*Me*$_2$), 1.32 (t, J = 7.0 Hz, CH_3), 2.86 (sept, J = 7.0 Hz, C*H*Me$_2$), 3.76 and 3.82 (2s, $2OCH_3$), 3.67 (d, J = 1.5 Hz, CH), 4.12 (d, J = 1.5 Hz, CH), 4.24–4.34 (m, OCH_2) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 14.01 (CH_3), 17.67 and 17.68 (CH*Me*$_2$), 40.89 (*C*HMe$_2$), 44.42 and 50.30 (2CH), 52.27 and 52.65 ($2OCH_3$), 61.71 (OCH_2), 140.65 and 143.06 (C=C), 159.78, 160.02, and 169.80 (3C=O ester), 209.13 (C=O) ppm.

Triethyl 4-isobutyrylcyclobut-1-ene-1,2,3-tricarboxylate (**3h**, $C_{17}H_{24}O_7$)

Pale yellow oil, yield 0.62 g (91%); IR (KBr): $\bar{\nu}$ = 1728 and 1708 (C=O), 1645 (C=C) cm^{-1}; MS: m/z (%) = 341 ($M^+ + 1$, 6), 295 (23), 250 (38), 224 (75), 150 (44), 73 (100).

Major isomer (*cis*-**3h**) (60%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.12 and 1.22 (2d, J = 7.1 Hz, CH*Me*$_2$), 1.22–1.35 (3t, J = 7.0 Hz, $3CH_3$), 2.86 (sept, J = 7.1 Hz, C*H*Me$_2$), 3.98 (d, J = 5.5 Hz, CH), 4.04 (d, J = 5.5 Hz, CH), 4.10–4.31 (m, $3OCH_2$) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 14.04, 14.05, and 14.06 ($3CH_3$), 17.23 and 18.71 (CH*Me*$_2$), 38.83 (*C*HMe$_2$), 44.87 and 45.11 (2CH), 61.38, 61.53, and 61.57 ($3OCH_2$), 136.10 and 148.47 (C=C), 159.62, 168.29, and 169.22 (3C=O ester), 200.50 (C=O) ppm.

Minor isomer (*trans*-**3h**) (40%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16 and 1.17 (2d, J = 7.1 Hz, CH*Me*$_2$), 1.22–1.35 (3t, J = 7.0 Hz, $3CH_3$), 3.60 (sept, J = 7.1 Hz, C*H*Me$_2$), 3.74 (d, J = 1.25 Hz, CH), 3.75 (d, J = 1.25 Hz, CH), 4.10–4.31 (m, $3OCH_2$) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 14.10, 14.11, and 14.12 ($3CH_3$), 17.66 and 17.84 (CH*Me*$_2$), 40.91 (*C*HMe$_2$), 45.64 and 50.14 (2CH), 61.35, 61.38, and 61.41 ($3OCH_2$), 141.21 and 142.56 (C=C), 159.90, 160.10, and 168.59 (3C=O ester), 209.29 (C=O) ppm.

Di-tert-butyl 4-isobutyryl-1-(ethoxycarbonyl)cyclobut-1-ene-2,3-dicarboxylate (**3i**, $C_{21}H_{32}O_7$)

Pale yellow oil, yield 0.75 g (95%); IR (KBr): $\bar{\nu}$ = 1716 and 1704 (C=O), 1645 (C=C) cm^{-1}; MS: m/z (%) = 397 ($M^+ + 1$, 8), 352 (77), 251 (65), 195 (48), 163 (35), 71 (24), 57 (100).

Major isomer (*trans*-**3i**) (90%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.30 (t, J = 7.1 Hz, CH_3), 1.15 and 1.16 (2d, J = 7.0 Hz, CH*Me*$_2$), 1.48 and 1.52 (2s, $2OCMe_3$), 2.84 (sept, J = 7.0 Hz, C*H*Me$_2$), 3.55 (d, J = 2.0 Hz, CH), 4.03 (d, J = 2.0 Hz, CH), 4.24 (q, J = 7.1 Hz, OCH_2) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 14.11 (CH_3), 17.68 and 17.83 (CH*Me*$_2$), 27.89 and 27.99 ($2OCMe_3$), 40.79 (*C*HMe$_2$), 46.92 and 49.81 (2CH), 61.25 (OCH_2), 82.00 and 82.36 ($2OCMe_3$), 140.93 and 143.15 (C=C), 158.87, 160.03, and 168.35 (3C=O ester), 209.68 (C=O) ppm.

Minor isomer (*cis*-**3i**) (10%); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33 (t, J = 7.1 Hz, CH_3), 1.11 and 1.21 (2d, J = 7.1 Hz, CH*Me*$_2$), 1.46 and 1.50 (2s, $2OCMe_3$), 3.60 (sept, J = 7.0 Hz, C*H*Me$_2$), 3.60 (d, J = 5.5 Hz, CH), 3.90 (d, J = 5.5 Hz, CH), 4.31 (q, J = 7.1 Hz, OCH_2) ppm; ^{13}C NMR (125.7 MHz,

$CDCl_3$): $\delta = 14.10$ (CH_3), 17.27 and 18.79 (CH*Me*$_2$), 27.95 and 27.96 (2OC*Me*$_3$), 38.62 (*C*HMe_2), 45.67 and 45.83 (2CH), 61.12 (OCH_2), 81.80 and 81.88 (2O*C*Me_3), 136.54 and 148.48 (C=C), 160.27, 167.59, and 167.90 (3C=O ester), 200.26 (C=O) ppm.

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