Regioselective $Rh_2(OAc)_4$-Promoted Reactions of Methyl Diazoacetate with Terminal Triple Bond Enynes

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The selective $Rh_2(OAc)_4$-promoted methoxycarbonylmethylenation of a triple bond in enynes, with a terminal triple bond, by methyl diazoacetate is established, and the main factors, affecting the regioselectivity of the process, are elucidated. The easy *in situ* [2 + 2]-dimerization of methyl 1-alkenylcyclopropene-3-carboxylates in dimethyl *trans*-1,2-dialkenyltricyclo[3.1.0.0^{2,4}]hexane-3,6-dicarboxylates **2** is found, and their thermal rearrangement into dimethyl *trans*-1,2-dialkenylcyclohexa-1,4-diene-3,6-dicarboxylates **7** is also described.

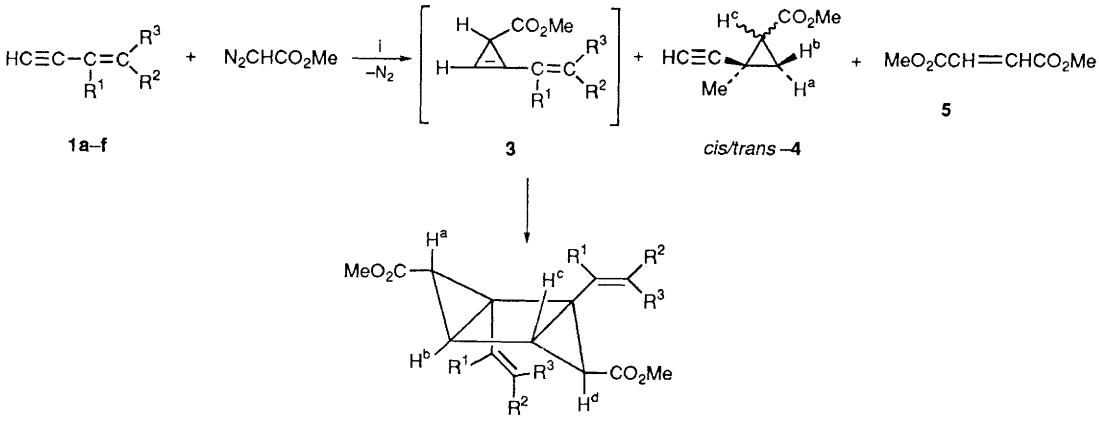
Alkenes and alkynes are known to react easily with alkyl diazoacetates (ADA) in the presence of Rh^{II} catalysts to yield cyclopropane- and cyclopropene-carboxylates respectively.[1] Meanwhile reactivities of double and triple bonds conjugated in enynes are unpredictable. Thus, in conjugated enynes with internal multiple bonds the double bonds are usually active,[2,3] though preferable alkoxycarbonylmethylenation of the triple bond has been observed in the case of unconjugated enynes.[4] Recently we have discovered[5] the selective methoxycarbonylmethylenation of the terminal triple bond of enynes in the course of $Rh_2(OAc)_4$-promoted deazotation of methyl diazoacetate (MDA) in the presence of but-3-en-1-yne **1a**. From this point of view it was interesting to find out if the selective methoxycarbonylmethylenation of the triple bond in **1a** has a general character. So, we have investigated the $Rh_2(OAc)_4$-promoted reactions of MDA with series of enynes **1b–h**, which have a terminal triple bond.

Results and Discussion

Experiments have been carried out in the presence of 0.2% mol of $Rh_2(OAc)_4$ in CH_2Cl_2 at 20–25 °C. To reach the complete conversion of MDA a 2.5–3.0-fold excess of enynes **1b–d** was used. In the case of low activity enynes **1e** and **g** the experiments were run with a 2.0–3.0-fold excess of MDA.

Enynes **1c–f** have been found to react with MDA in the same way as **1a**. With the exception of **1b** reactions proceeded selectively, involving only the triple bond, to afford up to 70% yields of dimethyl *trans*-1,2-dialkenyltricyclo[3.1.0.0^{2,4}]hexane-3,6-dicarboxylates **2c–f**, which are [2 + 2]-cycloadducts of the corresponding methyl 1-alkenylcyclopropene-3-carboxylates **3** (Scheme 1). The reaction of **1b** with MDA led to the corresponding **2b** in 46% yield alongside the double bond carbene adduct, methyl *cis*/*trans*-2-methyl-2-ethynylcyclopropanecarboxylate **4**, which was isolated in 25% yield. Enyne **1g** remained unchanged under these conditions; in this case MDA deazotation was accompanied by dimethyl fumarate and maleate **5** formation. In small quantities (< 15%), **5** was detected in all other enynes as well. Yields and properties of **2** are shown in Tables 1–3.

The structure of **2** was established on the basis of NMR spectroscopic data and by chemical transformations. Thus, the significantly lower field shifts of the magnetically equivalent H^a and H^d protons in **2** (δ 2.39–2.84), caused by magnetic anisotropy of cyclopropane rings,[6] in comparison with those of the cyclopropanecarboxylates (δ 1.7–2.1) indicate an in-plane position of these protons, with respect to the neighbouring cyclopropane rings, that accords well with the chair conformation of the tricyclohexane fragment. Additional evidence for the chair conformation is the low value of $J_{bc} \sim 0$ Hz, obtained from ^{13}C satellite spectra of H^b in **2a**, **c**. This observation corresponds well to the expected value for the vicinal coupling constant of tricyclohexane, as the dihedral angle H^b–C–C–H^c in the chair conformation for such polycycles is close to 90° (see ref. 7). The low values of the coupling constants $J_{ab} = J_{cd} = 1.0$–2.0 Hz testify accordingly[8] a *trans*-arrangement of the corresponding protons and as a result a *trans*-arrangement of the CO_2Me groups.



2a–f

a, $R^1 = R^2 = R^3 = H$; **b**, $R^1 = Me$, $R^2 = R^3 = H$; **c**, $R^1 = H$, $R^2 = R^3 = Me$; **d**, $R^1 + R^2 = (CH_2)_4$, $R^3 = H$; **e**, $R^1 = Ph$, $R^2 = R^3 = Me$; **f**, $R^1 = R^3 = H$, $R^2 = CO_2Me$; **g**, $R^1 = CO_2Me$, $R^2 = H$, $R^3 = Me$

Scheme 1 *Reagents and conditions:* i, $Rh_2(OAc)_4$, 20 °C, CH_2Cl_2

Table 1 Properties of compounds **2a–f** and **7c** and **d**

Compd.	Yield (%)[a]	M.p./°C	ν(KBr)/cm^{-1}	*m/z* (%)
2a	70	100–105 (decomp.)	1720 (C=O), 1628 (C=C)	248 (M^+, 0.3), 216 (3), 189 (28), 157 (78), 130 (50), 129 (100), 115 (55), 105 (27)
2b	46[b]	Oil[c]	1736 (C=O),[d] 1639 (C=C)	276 (M^+, 0.6), 244 (9), 217 (24), 201 (12), 186 (15), 185 (100), 184 (10), 169 (14), 158 (28), 157 (71), 143 (71)
2c	67	94–97	1728 (C=O) 1670 (C=C)	304 (M^+, 3), 272 (7), 245 (31), 229 (18), 213 (49), 203 (41), 197 (22), 189 (53), 171 (60), 157 (37), 143 (58)
2d	11	60–62	1732 (C=O), 1643 (C=C)	356 (M^+, 1), 324 (6), 297 (20), 265 (69), 237 (43), 195 (48), 186 (83), 165 (38), 155 (54), 141 (55), 128 (67)
2e	25	Oil[e]	1724 (C=O),[d] 1645, 1597 (C=C)	456 (M^+, 3), 424 (7), 365 (11), 321 (10), 279 (14), 203 (13), 202 (16), 165 (10), 131 (54), 129 (20), 119 (72)
2f	27	150–152	1732, 1720 (C=O), 1639 (C=C)	273 (10), 245 (10), 213 (21), 171 (32), 155 (23), 143 (12), 142 (20), 129 (13), 128 (38), 127 (24), 115 (21), 112 (11)
7c	100	58–60	1732 (C=O), 1655, 1635 (C=C)	304 (M^+, 24), 272 (13), 246 (18), 245 (100), 229 (25), 213 (90), 203 (66), 197 (22), 189 (93), 185 (27), 171 (93)
7d	86	112–116	1734 (C=O), 1649, 1624 (C=C)	356 (M^+, 4), 324 (4), 297 (13), 265 (31), 237 (17), 195 (20), 186 (36), 165 (22), 155 (18), 141 (30), 128 (22)

[a] Preparative yields. [b] A 25% yield of **4** was also obtained. [c] n_D^{20} 1.4947; [d] Taken in film. [e] n_D^{20} 1.5530.

Table 2 ^{1}H NMR parameters of compounds **2a–f** and **7a–d, f**

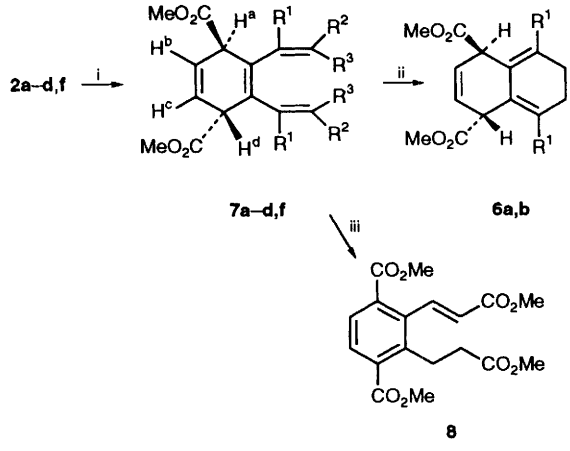
	δ_H($CDCl_3$)						*J*/Hz			
Compd.	H^a	H^b	R^1	R^2	R^3	OMe	J_{ab}	$J_{R^1R^2}$	$J_{R^1R^3}$	$J_{R^2R^3}$
2a[a]	2.69 (d)	2.27 (d)	5.81 (dd)	5.21 (dd)	5.41 (dd)	3.68 (s)	1.5	10.8	17.5	1.9
2b[a]	2.71 (d)	2.33 (d)	1.82 (br s)	5.00 (m)	4.81 (m)	3.61 (s)	1.1	1.5	1.0	—
2c[a]	2.66 (d)	2.18 (d)	5.25 (m)	1.70 (br s)	1.70 (br s)	3.62 (s)	1.5	1.5	1.0	—
2d[a]	2.59 (d)	2.25 (d)	2.00 (m, 4 H, $=CCH_2$) 1.55 (m, 4 H, CH_2CH_2)		5.50 (m)	3.57 (s)	1.0	—	—	—
2e[b]	2.39 (d)	2.10 (d)	7.31 (br s)	2.02 (s)	1.52 (s)	3.55 (s)	1.0	—	—	—
2f[b]	2.83 (d)	2.55 (d)	6.92 (d)	3.75 (s)	6.09 (d)	3.75 (s)	2.0	—	16.0	—
7a[b]	4.23 (d)	5.94 (d)	6.95 (dd)	5.24 (d)	5.28 (d)	3.66 (s)	1.5	11.5	17.5	—
7b[b]	4.10 (d)	5.89 (d)	1.89 (br s)	4.93 (m)	4.80 (m)	3.65 (s)	1.3	1.5	1.0	2.0
7c[a]	3.88 (m)	5.89 (m)	5.47 (m)	1.69 (br s)	1.53 (br s)	3.66 (s)	—	1.5	1.0	—
7d[b]	4.10 (d)	5.89 (d)	2.00 (m, 4 H, $=CCH_2$) 1.56 (m, 4 H, CH_2CH_2)		5.50 (m)	3.63 (s)	1.2	—	—	—
7f[b]	4.25 (d)	5.98 d	8.00 (d)	3.77 (s)	6.02 (d)	3.65 (s)	1.5	—	16.0	—

[a] Taken at 250 MHz. [b] Taken at 90 MHz.

The correct conclusion about the mutual arrangement of alkenyl substituents in **2** cannot be made on the basis of NMR spectroscopic data. So, we have tried, as it was done[5] for **2a**, to carry out the thermal isomerization of **2b–f** into dimethyl 1,4,6,7-tetrahydronaphthalene-1,4-dicarboxylates **6**, which is possible only in the case of vicinal alkenyl groups. However, only **2b** appeared to be isomerized into **6b** with 98% yield after 2.5 h refluxing in *m*-xylene at 144 °C; as a result of electrocyclic reaction dimethyl *trans*-1,2-di(1-methylethenyl)cyclohexa-1,4-dien-3,6-dicarboxylate **7b** was initially formed (Scheme 2).

The tricyclohexanes **2c** and **d** were found to be transformed into the cyclohexadienes **7c** and **d**, which were stable under these conditions and have been isolated as individual compounds and characterized by spectroscopic data (Tables 1–3). The vicinal arrangement of alkenyl groups in **7c** and **d** has been proved by observation of the *cis*-vicinal coupling J_{bc} in ^{13}C-satellite spectra of H^b. The remarkably high value of the constant (10 Hz) shows unequivocally the location of alkenyl substituents at positions 1 and 2 of **7c** and **d**, and consequently their vicinal arrangement in **2c** and **d**. The tricyclohexane **2f** underwent the same isomerization to **7f**, but in the course of isolation by column chromatography on SiO_2 it was aromatized completely into methyl 2,5-di(methoxycarbonyl)-6-[2-(methoxycarbonyl)-ethyl]cinnamate **8**, which can be considered to be correct evidence for structure **2f** as well. Among the studied compounds **2** only **2e** did not undergo the isomerization and was stable even after 5 h refluxing in nonane at 150 °C.

The examples of thermal [2 + 2]-cyclodimerization of 1-alkenylcyclopropene-3-carboxylates are not known. Moreover, 1,2-disubstituted cyclopropene-3-carboxylates are stable under similar conditions.[3,9] The only example of such transformation



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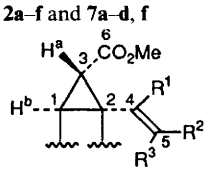
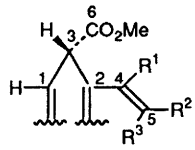
Scheme 2 *Reagents and conditions:* i, ii reflux, toluene or xylene, 2.5–10 h; iii SiO_2, 20 °C

Table 3 ^{13}C NMR parameters[a] of compounds **2a–f** and **7a–d, f**



2a–f

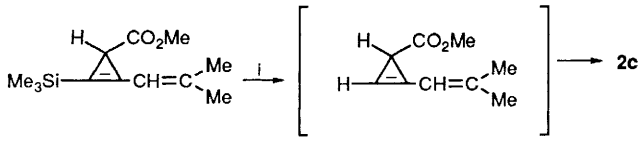


7a–d,f

Compd.	δ_C C-1	C-2	C-3	C-4	C-5	C-6	OMe	R^1	R^2	R^3
2a	30.24	40.70	42.91	129.81	117.24	169.25	51.64	—	—	—
2b	27.75	45.90	41.62	137.94	116.54	165.87	51.20	22.06	—	—
2c	28.72	40.86	42.70	116.11	138.86	169.20	51.09	—	25.80	18.65
2d	26.83	46.60	41.13	130.62	127.70	168.82	50.77	28.13, 24.93 (=CCH_2), 22.44, 21.84 (CH_2CH_2)		—
2e	28.78	45.08	43.51	127.81	137.07	169.79	51.20	143.52, 129.65, 128.08, 126.29	22.28, 21.46	
2f	32.57	39.18	44.06	139.89	122.88	168.11	51.64	—	52.23 (OMe), 166.05 (CO)	—
7a	123.85	129.38	44.65	132.57	115.59	171.82	51.91	—	—	—
7b	124.18	131.87	47.25	144.22	115.02	171.85	51.85	22.22	—	—
7c	124.61	128.62	47.74	122.88	135.39	172.34	51.91	—	25.53	19.35
7d	124.61	132.25	47.52	137.45	125.91	172.61	51.96	28.40, 25.47 (=CCH_2), 23.03, 22.22 (CH_2CH_2)		—
7f	123.80	133.44	45.35	139.07	121.52	171.14	51.91	—	52.83 (OMe), 166.59 (CO)	—

[a] Recorded in $CDCl_3$ at 22.5 MHz.

in other classes of alkenylcyclopropenes is 'head-to-head' [2 + 2]-cyclodimerization of 1-vinylcyclopropene.[10] To prove the tricyclohexane **2** formation, as a result of [2 + 2]-cyclodimerization of cyclopropene **3**, we have undertaken the alternative synthesis of **3** by hydrolytic desilylation of methyl 1-trimethylsilyl-2-(2-methylprop-1-enyl)cyclopropene-3-carboxylate **9**, which we have recently prepared.[9] This method is known to have been developed earlier for the synthesis of cyclopropene-3-carboxylate from 1-trialkylsilylcyclopropene-3-carboxylates.[11] However, the treatment of **9** with KF in aqueous DMF at 20 °C gave not **3c** but the corresponding **2c** in 87% yield (Scheme 3). This result shows the extremely high

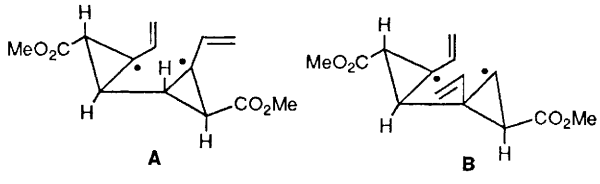


9 **3c** **2c**

Scheme 3 *Reagents and conditions:* i, KF, 25 °C, DMF–H_2O

activity of **3** in the thermal [2 + 2]-cyclodimerization and explains their absence in catalytic MDA-enyne reactions.

In our opinion there are two main reasons for the stereospecific proceeding of thermal [2 + 2]-cyclodimerization of **3**: an additional stabilization of radical centres in 'head-to-head' biradical **A** by vinyl groups in comparison with 'head-to-tail' biradical **B**; both of them are probable intermediates for

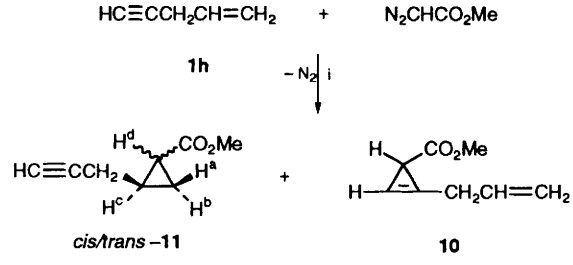


A **B**

such cyclopropene transformations,[10] and steric demands provided with cyclopropane fragments and CO_2Me groups for biradical cyclization.

Yields of products given in Table 3 show a remarkable influence of the conjugation effect and double bond substitution on the regioselectivity of the $Rh_2(OAc)_4$-promoted MDA-enyne reaction.

Indeed, in contrast with conjugated enynes, pent-4-en-1-yne **1h** having isolated double and triple bonds, reacts with MDA at



1h *cis/trans*-**11** **10**

Scheme 4 *Reagents and conditions:* i, $Rh_2(OAc)_4$, 20 °C, CH_2Cl_2

both multiple bonds resulting in methyl 1-(prop-2-enyl)cyclopropene-3-carboxylate **10** and methyl *cis*/*trans*-1-(prop-2-ynyl)cyclopropanecarboxylates **11** (*cis*/*trans* = 1:1) in **10**:**11** ratio 58:42 with 65% total yield.

These data indicate a significant difference between the double bond activity in unconjugated enynes and conjugated ones, that is probably the main reason for a high regioselectivity of conjugated enynes **1** in cyclopropenation.

Substituents at the double bonds affect the regioselectivity of MDA-enyne reactions in the similar way as they do in the reactions of ADA with 1,3-dienes. So a Me-substituent at C-3 caused the cyclopropanation of the adjacent double bond in 1,3-dienes,[12] the same orientation effect is displayed in the case of **1b**, resulting in a significant quantity of **4** being formed. In accordance with data[12] terminal Me-substituents drastically decrease the activity of the double bond in enynes **1c** and **e**, in spite of activated effect of Ph at C-3 in the last case. The low activity of enynes **1f** and **g** containing an electron-withdrawing CO_2Me substituent is quite obvious. To a large extent the effect of the CO_2Me group reveals an internal location that induces the complete deactivation of the triple bond as well. The steric effects of substituents are demonstrated well in the case of enyne

1d. The bulky tetramethylene bridge hinders the attack of the Rh(II)-carbene complex and decreases the reactivity of both double and triple bonds.

Experimental

General Methods.—M.p.s were determined on a Kofler block and are uncorrected. IR spectra were measured on a Bruker IFS-113V spectrometer. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions at 90 and 22.5, and 300 and 75 MHz, respectively on JEOL FX 90Q and Bruker AW-300 instruments. Some ^1H NMR spectra were run at 250 MHz on a Bruker WM-250 instrument. Tetramethylsilane was used as the internal reference. The mass spectra were taken at 70 eV on a quadruple chromatomass-spectrometer, Finnigan INCOS-50. For GLC-analysis an OV-1501 column (0.25 mm × 30 m) was used. Chromatographic columns were filled with CHEMAPOL *L* silica gel (40–100 mesh). A solvent system of hexane–ether 6:1 (v/v) was used for product isolation. SILUFOL plates were applied for TLC.

But-3-en-1-yne **1a** and 3-methylbut-3-en-1-yne **1b** of commercial grade purity were used. 1-Ethynylcyclohexene **1d**, methyl (*E*)-pent-2-en-4-ynoate **1f** and methyl (*E*)-pent-3-en-1-yn-3-ylcarboxylate were prepared according to the known procedures.[13–15]

4-*Methylpent*-3-*en*-1-*yne* **1c**.—To an intensively stirred warm (50 °C) dispersion of Na powder (27.4 g, 1.19 mol) in nonane (150 cm^3) of commercial grade purity 1,1-dichloro-4-methylpent-1,3-diene (46.8 g, 0.31 mol) was added dropwise during 4–5 h. A temperature of 50–60 °C was kept during the whole period of addition. The reaction mixture was cooled to 20 °C and was carefully treated with H_2O (200 cm^3). The organic layer was separated and the crude product was distilled off at 50–95 °C and was redistilled after drying with anhydrous Na_2SO_4 to give **1c** (16.9 g, 68%), b.p. 80–82 °C (lit.,[16] 73–75 °C), n_D^{20} 1.4475; ν_{max}(film)/cm^{-1} 3325 (≡C–H), 2098 (C≡C) and 1635 (C=C); δ_H(250 MHz) 5.25 (1 H, m, =CH, $^4J_{trans}$ 1.0, $^4J_{cis}$ 1.5), 2.99 (1 H, br s, ≡CH, ^4J 2.5), 1.93 (3 H, s, *cis*-Me) and 1.82 (3 H, s, *trans*-Me); δ_C(22.5 MHz) 150.33 (C), 104.56 (HC=), 81.80 (≡C–), 79.20 (HC≡), 24.70 (*trans*-Me) and 20.86 (*cis*-Me).

4-*Methyl*-3-*phenylpent*-3-*en*-1-*yne* **1e**.—To a cooled (0 °C) solution of HC≡CMgBr (0.7 mol) in THF (300 cm^3) 2-methyl-1-phenylpropan-1-one (74.0 g, 0.50 mol) was added dropwise during 1.5 h. The mixture was stirred for 3 h at 20 °C and then treated with NH_4Cl solution (500 cm^3). The upper organic layer was separated, the water layer was extracted with ether (2 × 150 cm^3). Extracts were combined with the organic layer. After removal of solvents a residue was diluted with ether, dried (anhydrous Na_2SO_4) and evaporated *in vacuo*. A residue was distilled to give 4-methyl-3-phenylpent-1-yn-3-ol (84.4 g, 97%), b.p. 82 °C/0.3 mmHg.

Through a heated (250 °C) quartz tube (1 × 17 cm) filled with anhydrous $MgSO_4$ (10 cm^3) and evacuated to 15 mmHg, 4-methyl-3-phenylpent-1-yn-3-ol (10.0 g, 57.0 mmol) was passed in 1.5 h. A crude product (5.98 g) was separated using a chromatographic column (CC) eluted with hexane (200 cm^3) to yield **1e** (5.07 g, 57%), b.p. 62–64 °C/0.5 mmHg, n_D^{20} 1.5615; ν_{max}(film)/cm^{-1} 3300 (≡C–H), 2089 (C≡C), 1618 (C=C), 1576 and 1597 (Ph); δ_H(90 MHz) 7.30 (5 H, s, Ph), 3.16 (1 H, br s, ≡CH), 2.14 and 1.80 (6 H, br s, 2 Me); δ_C(75 MHz) 144.58 (Me_2C=), 139.06, 129.09, 128.10, 126.91 (Ph), 118.24 (C), 84.36 (≡C–), 80.13 (HC≡), 23.87 and 21.41 (2 Me); *m*/*z* 156 (M^+, 49%), 141 (40), 128 (12), 115 (46), 91 (7) and 77 (12).

General Procedure for Rh^{II}*-Promoted Interaction of Methyl Diazoacetate* (*MDA*) *with Enynes* **1**.—To an intensively stirred solution of enyne **1** (0.30 mol) in abs. CH_2Cl_2 (100 cm^3) green crystals of $Rh_2(OAc)_4$ (0.10 g, 0.23) mmol) were added. A green solution was formed immediately. To the coloured mixture a solution of MDA (0.10 mol) in abs. CH_2Cl_2 (50 cm^3) was added dropwise during 8 h and stirred at the same temperature (20 °C) for an additional 0.5 h. After evaporation of a solvent dimethyl *anti*-1,2-dialkenyltricyclo[3.1.0.$0^{2,4}$]hexan-3,6-dicarboxylates **2** were separated from a residue by CC. The properties of **2** are presented in Tables 1–3.

Methyl cis/trans-2-*methyl*-2-*ethynylcyclopropanecarboxylate* **4** was isolated as a mixture (1:1) of *cis*/*trans*-isomers with b.p. 70–75 °C/20 mmHg by distillation of the corresponding reaction mixture at 70 °C (bath temperature)/0.5 mmHg before **2b** separated, **4** being collected into a cooled (−30 °C) trap. The individual isomers were separated by CC. *trans*-**4**, n_D^{20} 1.4565; ν_{max}(film)/cm^{-1} 3294 (≡C–H), 2117 (C≡C) and 1732 (C=C); δ_H(250 MHz) 3.72 (3 H, s, OMe), 2.09 (1 H, dd, H^c, J_{bc} 8.5, J_{ac} 6.5), 1.94 (1 H, s, ≡CH), 1.42 (3 H, s, Me), 1.38 (1 H, dd, H^b, J_{ab} 4.5) and 1.29 (1 H, dd, H^a); δ_C(22.5 MHz) 170.66 (C=O), 88.21 (–C≡), 64.86 (HC≡), 51.58 (OMe), 27.64 (CH^c), 21.95 (CH_2), 17.29 (Me) and 16.10 (C); *m*/*z* 138 (M^+, 23%), 123 (47), 110 (23), 109 (11), 107 (27), 96 (22), 95 (32), 87 (16), 83 (22), 80 (10), 79 (53), 78 (27) and 77 (95). *cis*-**4**, n_D^{20} 1.4590; ν_{max}(film)/cm^{-1} 3290 (≡C–H), 2117 (C≡C) and 1736 (C=C); δ_H(250 MHz) 3.73 (3 H, s, OMe), 2.02 (1 H, s, ≡CH), 1.77 (1 H, dd, H^c, J_{ac} 8.0, J_{bc} 6.5), 1.62 (1 H, dd, H^b, J_{ab} 4.5), 1.41 (3 H, s, Me) and 1.07 (1 H, dd, H^a); δ_C(22.5 MHz) 170.33 (C=O), 84.41 (–C≡), 67.51 (HC≡), 51.58 (OMe), 28.88 (CH^c), 24.71 (CH_2), 21.90 (Me) and 16.70 (C); *m*/*z* the same as for *trans*-**4**.

Methyl 2-*prop*-2-*enylcyclopropene*-3-*carboxylate* **10** *and methyl* cis/trans-2-*prop*-2-*ynyl*-*cyclopropanecarboxylate* **11**.—The interaction of **1h** with MDA was run according to the general procedure. After MS-GC-analysis the reaction mixture was separated by CC into the cyclopropene **10** (37%) as a viscous oil, n_D^{20} 1.4798; ν_{max}(film)/cm^{-1} 1828 (cyclo-C=C), 1728 (C=O) and 1639 (C=C); δ_H(250 MHz) 6.46 (1 H, m, HC=, cyclo, ^3J 1.7, ^4J 1.5), 5.87 (1 H, m, HC=, $^3J_{cis}$ 10.1, $^3J_{trans}$ 16.5, ^3J 6.2), 5.21 (1 H, dm, *cis*-H, $=CH_2$, ^2J 1.8, ^4J 1.6), 5.14 (1 H, dm, *trans*-H, $=CH_2$, ^4J 1.6), 3.66 (3 H, s, OMe), 3.27 (2 H, dm, CH_2) and 2.20 (1 H, d, CH, cyclo); δ_C(22.5 MHz) 176.83 (C=O), 131.89 (CH=), 117.53 (CH_2=), 113.62 (C), 95.37 (CH=, cyclo), 51.86 (OMe), 29.27 (CH_2) and 19.64 (CH); *m*/*z* 137 ([M − 1]$^+$, 4%), 123 (12), 111 (4), 107 (7), 95 (13), 79 (100) and 77 (87); and a mixture (1:1) of cyclopropanes *cis*/*trans*-**11** (28%), as an oil, ν_{max}(film)/cm^{-1} 3332 (H–C=), 2121 (C≡C) and 1751 (C=O); *m*/*z* ([M − 1]$^+$, 2%), 109 (7), 107 (22), 95 (20), 80 (12), 79 (100), 78 (63), 77 (97), 67 (15) and 59 (40); δ_H(300 MHz) for *cis*-**11** 3.71 (3 H, s, OMe), 2.56 (1 H, ddd, CH_2, ^2J 17.0, ^3J 6.5), 2.42 (1 H, ddd, CH_2, ^3J 7.5), 1.98 (1 H, t, CH≡, ^4J 2.5), 1.80 (1 H, ddd, H^d, J_{dc} 8.3, J_{db} 7.8, J_{da} 5.5), 1.57 (1 H, m, H^c), 1.14 (1 H, ddd, H^b, J_{ab} 4.5, J_{bc} 8.1) and 1.03 (1 H, ddd, H^a, J_{ac} 6.8); for *trans*-**11** 3.69 (3 H, s, OMe), 2.45 (2 H, m, CH_2), 1.98 (1 H, t, HC≡, ^4J 2.5), 1.65 (1 H, ddd, H^d, J_{da} 9.0, J_{db} 6.1, J_{dc} 4.0), 1.60 (1 H, m, H^c), 1.20 (1 H, ddd, H^a, J_{ab} 4.3, J_{ac} 4.6) and 0.98 (1 H, ddd, H^b, J_{bc} 8.5); δ_C(22.5 MHz) for *cis*-**11** 172.47 (C=O), 82.68 (–C≡), 68.22 (HC≡) 51.29 (OMe), 19.97 (CH^c), 17.51 (CH^d), 16.56 (CH_2) and 13.47 (CH_2, cyclo); for *trans*-**11** 173.80 (C=O), 80.19 (–C≡), 69.68 (HC≡), 51.29 (OMe), 20.38 (CH_2), 19.27 (CH^c), 18.40 (CH^d) and 13.47 (CH_2, cyclo).

Dimethyl trans-5,8-*Dimethyl*-1,4,6,7-*tetrahydronaphthalene*-1,4-*dicarboxylate* **6b**.—A solution of **2b** (0.42 g, 1.52 mmol) in *m*-xylene (4 cm^3) was refluxed for 2.5 h. The solvent was evaporated and the residue was purified by CC to afford **6b** (0.41 g, 98%) as a yellow oil, n_D^{20} 1.5248; ν_{max}(film)/cm^{-1} 1732 (C=O) and 1651 (C=C); δ_H(90 MHz) 5.90 (2 H, d, HC=, ^3J 2.2), 4.19 (2 H, d, HC), 3.67 (6 H, s. OMe), 2.21–1.85 (4 H, m, CH_2) and

1.80 (6 H, s, Me); δ_C(22.5 MHz) 172.61 (C=O), 130.89 (C-5 and -8), 124.72 (C-2 and -3), 122.12 (C-9 and -10), 51.80 (OMe), 43.46 (C-1 and -4), 29.59 (C-6 and -7) and 19.40 (Me); *m/z* 276 (M^+, 1%), 261 (2), 245 (3), 244 (2), 217 (8), 215 (10), 199 (9), 173 (8), 157 (20), 141 (11), 128 (13), 115 (17) and 105 (11).

Dimethyl trans-1,2-*Di*(2-*methylprop*-1-*enyl*)*cyclohexa*-1,4-*diene*-3,6-*dicarboxylate* **7c** *and Dimethyl* trans-1,2-*Di*(*cyclohex*-1-*enyl*)*cyclohexa*-1,4-*diene*-3,6-*dicarboxylate* **7d**.—A solution of **2c** (0.50 g, 1.64 mmol) in toluene (5 cm^3) was refluxed for 3 h. A solvent was evaporated and the residue was purified by CC to afford **7c** (0.50 g, ~100%) as crystals. In a similar way, **2d** (70 mg, 0.2 mmol) gave **7d** (60 mg, 86%) as crystals upon refluxing in *m*-xylene (3 cm^3) for 4 h. The properties of **7c** and **d** are presented in Tables 1–3.

Methyl 2,5-*Di*(*methoxycarbonyl*)-6-(2-*methoxycarbonylethyl*)*cinnamate* **8**.—By the same procedure **2f** (25 mg, 0.07 mmol) was converted into **7f** (toluene, 2 cm^3, reflux, 3 h). The NMR spectra were taken for a raw material (Tables 2, 3) and the oil (30 mg) was eluted through a column filled with silica gel by the solvent mixture to yield **8** (22 mg, 88%) as a white solid, ν_{max}(film)/cm^{-1} 1728 (C=O) and 1647 (C=C); δ_H(300 MHz) 8.07 (1 H, d, HC=, ^3J 16.1), 7.84 and 7.70 (2 H, 2 d, HC, Ar, ^3J 8.1), 5.89 (1 H, d, =CHCO), 3.95, 3.88, 3.84 and 3.72 (12 H, 4 s, OMe), 3.24 (2 H, m, CH_2) and 2.56 (2 H, m, CH_2CO); δ_C(75 MHz) 172.79 (C=O, Ar), 167.42, 166.07 (C=O), 143.21 (*HC*=CHCO), 140.27, 137.21, 134.24, 134.00 (C=C, Ar), 130.18, 127.63 (HC=*CH*, Ar), 124.32 (HC=*C*HCO), 52.61 (OMe, Ar), 51.95, 51.77 (OMe), 34.39 (CH_2) and 26.07 (CH_2CO).

An Alternative Synthesis of **2c** *by Desilylation of Methyl* 1-*Trimethylsilyl*-2-(2-*methylprop*-1-*enyl*)*cyclopropene*-3-*carboxylate* **9**.—To a stirred solution of $KF\cdot 2H_2O$ (0.42 g, 4.47 mmol) in DMF (5 cm^3) and water (0.5 cm^3), **9** (0.67 g, 3.0 mmol) was added at 25 °C. The mixture was stirred at the same temperature for 1.5 h, diluted with NH_4Cl solution (50 cm^3) and extracted with ether (2 × 30 cm^3). Combined extracts were washed with NH_4Cl solution (3 × 50 cm^3) and were dried (Na_2SO_4). Solvents were evaporated and a residue was purified by CC to afford **2c** (0.39 g, 86%) as a white solid.

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