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Rhodium(I)-catalyzed [3+2+2]-cyclization of alkenyl Fischer carbene complexes with methyl buta-2,3-dienoate

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ABSTRACT

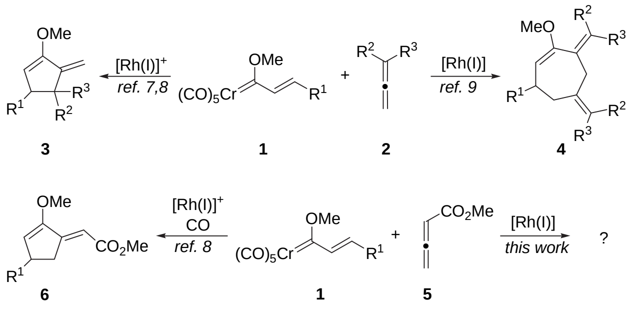
A variety of alkenyl chromium Fischer carbene complexes react with methyl buta-2,3-dienoate in the presence of a rhodium catalyst to afford substituted cycloheptene derivatives **7**, along with minor amounts of cyclopentene derivatives **6**. Through this [3+2+2]-cyclization two allene units and one alkenyl carbene ligand are assembled in a selective manner.

1. Introduction

Fischer carbene complexes of group 6 metals are valuable tools in stoichiometric transition metal-mediated organic synthesis since they feature a variety of interesting and unique reaction modes.[1] In a number of cases, complex structural frameworks, hardly accessible by traditional methodologies, become available in a single step by using these metal reagents. Despite their synthetic potential, studies concerning these compounds were restricted mainly to readily available, fairly stable group 6 metal complexes. Recently, we and others have reported on new metal carbenes of groups 9–11 by the chromium-metal exchange reaction.[2] In particular, we were able not only to isolate and characterized by X-ray analysis new rhodium(I) carbenes, but also to find that they feature a divergent reactivity with respect to that of parent chromium carbenes.[3]

Doubtless, the reaction with unsaturated carbon-based substrates -cyclopropanation of alkenes and the annulation with alkynes (Dötz reaction)- constitutes the basic C–C bond-forming reactions using group 6 carbene complexes. On the contrary, the reactivity of these carbenes toward allenes, whose potential for C–C bond formation has been well established over the last few years,[4] has been much less explored.[5]

Recently, we become involved in the study of the reactivity of Fischer carbene complexes with neutral and activated allenes in the presence of catalytic amounts of rhodium(I) (Scheme 1). Interestingly, we found not only a differential reactivity compared with the uncatalyzed reaction,[6] but the reaction course can be finely modulated depending on the electronic demand of the allene substrate by appropriate choice of the rhodium(I) catalyst (Scheme 1). Thus, neutral and electron-rich allenes **2** afforded the [3+2] cycloadduct **3** upon reaction with carbenes **1** in the presence of either the cationic complex [Rh(cod)(naphthalene)][SbF$_6$] (Wender catalyst) or the neutral complex [Rh(CO)$_2$Cl]$_2$ under CO atmosphere.[7,8] In a complementary fashion, the use of the neutral complex [Rh(cod)Cl]$_2$ resulted in the formation of the [3+2+2] cycloadduct **4**.[9] Finally, initial results with electron-poor allenes **5** revealed that the [3+2] cycloadduct **6** was formed using the cationic Wender catalyst under CO atmosphere.[8] Interestingly, the



Scheme 1.

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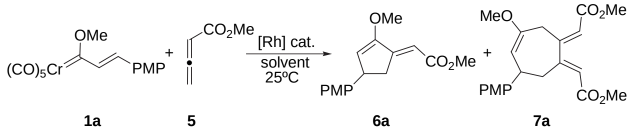
chemoselectivity of the cyclization was again complementary to that observed with electron-rich allenes (the terminal and internal C═C bond of the allene, respectively were involved).

Taking into consideration the intrinsic interest of the complete process as well as the significance of the resulting cycloadducts (cyclopentenone and cycloheptanone precursors) we report herein our studies of the rhodium-catalyzed reaction of chromium carbenes **1** and methyl 2,3-butadieoate **5** that establish a protocol for a new three-component heptannulation reaction.

2. Results and discussion

Previously, it was found that the reaction of carbene complex **1a** (R^1=4-MeO-C_6H_4) and methyl 2,3-butadienoate **5** using [Rh(cod)(naphthalene)][SbF_6] (10 mol %) under a CO atmosphere leads exclusively to the cycloadduct **6a**.[8] We have now observed that running this reaction in the absence of CO afforded a mixture of cyclopentene **6a** and cycloheptene **7a** (48 and 14% yield, respectively, after separation by column chromatography; Table 1, entry 1).

Table 1
Optimization for Rh(I)-catalyzed [3+2+2]-cyclization of alkenyl Fischer carbene complex **1a** with methyl 2,3-butadienoate **5**[a]



Entry	[Rh]	Solvent	6a[b] (%)	7a[b] (%)
1	[Rh(cod)($C_{10}H_8$)][SbF_6]	CH_2Cl_2	48	14
2	$[Rh(CO)_2Cl]_2$	CH_2Cl_2	42	28
3	$[Rh(CO)_2Cl]_2$	DMF	—[c]	—[c]
4	$[Rh(CO)_2Cl]_2$	MeCN	40	—
5	$[Rh(CO)_2Cl]_2$	THF	27	27
6	$[Rh(CO)_2Cl]_2$	DME	40	20
7	*$[Rh(CO)_2Cl]_2$*	*Dioxane*	*15*	*53*
8	$[Rh(cod)Cl]_2$	Dioxane	5	30
9	$Rh(PPh_3)_3Cl$	Dioxane	—[c]	—[c]
10	$Rh(PPh_3)_2(CO)Cl$	Dioxane	—[c]	—[c]
11	Rh(IMes)(cod)Cl	Dioxane	—[c]	—[c]

[a] Reaction conditions: **1a** (0.5 mmol), **5** (1.5 mmol), [Rh] (10 mol %), solvent (10 mL), 25 °C, 4–24 h.

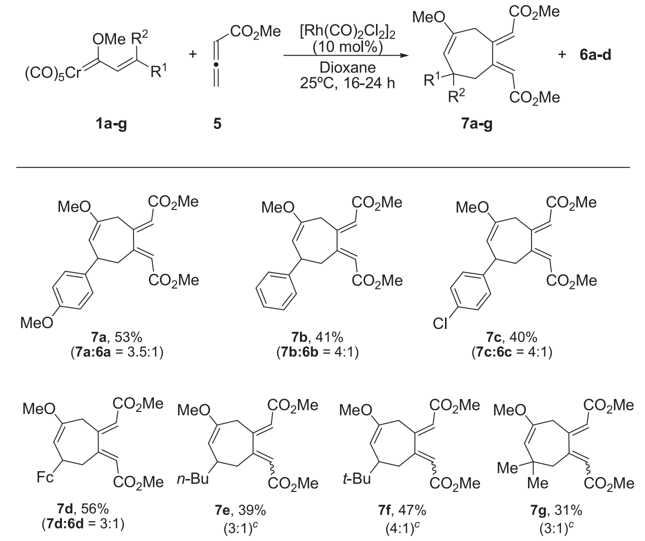
[b] Yield of isolated products after chromatographic separation (SiO_2, hexane/ethyl acetate, 3:1 v/v).

[c] A complex mixture of unidentified compounds was obtained.

Despite that a **6a**/**7a** mixture was indeed formed it is relevant that the formation of the [3+2+2] cycloadduct **7a** occurs in a chemo-, regio- and stereoselective manner. Therefore, further efforts were made in order to uncover this particular heptannulation reaction in a more efficient way. To achieve this goal several rhodium(I) catalysts and solvents were screened (see Table 1, entries 2–11). Firstly, the neutral catalyst $[Rh(CO)_2Cl_2]_2$ (10 mol %, CH_2Cl_2) afforded a mixture of **6a**/**7a** in moderate yield (**7a**, 28%) and selectivity (**6a**:**7a**=1.5:1) (Table 1, entry 2). Although this result seems rather modest, the enhancement of the selectivity toward **7a** proved the feasibility to control the reaction toward the cycloheptene derivatives. Thus, we tested a variety of solvents (Table 1, entries 2–7). Running the reaction in highly polar solvents either led to a complex mixture of unidentified products (DMF, entry 3) or gave exclusively **6a** (MeCN, entry 4). When ethereal solvents (THF, DME, dioxane) were used more promising results were reached in terms of yield and selectivity (entries 5–7), particularly in the case of dioxane (**7a**, 53%, **6a**/**7a**=1:3.5, entry 7). At this point, we observed a dual effect when the CO ligands of the catalyst were replaced with 1,5-cyclooctadiene (entry 8). Thus, using the catalyst $[Rh(cod)Cl_2]_2$, under the same reaction conditions, compound **7a** was formed with higher selectivity (**6a**/**7a**=1:6) albeit in lower yield (30%). On the other hand, other donor ligand-containing Rh(I)-catalysts tested (entries 9–11) did not provide satisfactory results since complex mixtures of unidentified compounds were obtained.

Accordingly, we decided to use $[Rh(CO)_2Cl_2]_2$ (10 mol %), as the optimal catalyst, in dioxane to accomplish the [3+2+2] cyclization with various chromium carbene complexes **1** (Table 2). Thus, when β-aryl substituted carbene complexes **1a**–**c** were reacted with methyl 2,3-butadienoate cycloheptenes **7a**–**c** were obtained in moderate yields, along with minor amounts of the corresponding cyclopentenes **6a**–**c**. Although the heptannulation reaction works for aryl substituents of different electronic nature, the presence of an electron-donating group (OMe) results in increasing the yield of the [3+2+2] cycloadduct. The presence of a second transition-metal on the carbene **1d** (Fc=ferrocenyl) has no significant effect on the reaction, affording **7d** in comparable yield and selectivity. Interestingly, the use of β-alkyl and β,β-dialkyl substituted carbene complexes led exclusively to the desired cycloheptene derivatives **7e**–**g**. In these cases, however, the *E,E* diastereoisomer was formed along with minor amounts of the *E,Z* diastereoisomer (from 3:1 to 4:1 ratio).[10] Unfortunately, this protocol seems restricted to monosubstiuted allenes like **5**. Thus, further attempts with 2,3-butadienoate methyl esters having an alkyl/aryl substituent at either C-2 or C-4 were unsuccessful.

Table 2
Rh(I)-catalyzed [3+2+2]-cyclization of alkenyl Fischer carbene complexes **1a-g** with methyl 2,3-butadienoate **5**[a,b]



7a, 53% (**7a**:**6a** = 3.5:1)
7b, 41% (**7b**:**6b** = 4:1)
7c, 40% (**7c**:**6c** = 4:1)
7d, 56% (**7d**:**6d** = 3:1)
7e, 39% (3:1)[c]
7f, 47% (4:1)[c]
7g, 31% (3:1)[c]

[a] Reaction conditions: **1a**–**g** (0.5 mmol), **5** (1.5 mmol), $[Rh(CO)_2Cl]_2$ (10 mol %), dioxane (10 mL), 25 °C, 16–24 h.

[b] Yields of isolated products.

[c] Obtained as a mixture of stereoisomers (estimated by ^1H NMR). Fc=Ferrocenyl.

The 1D- and 2D-NMR spectroscopic data of compounds **7a**–**g** are in agreement with their structure. Moreover, the structure of **7b** was unambiguously determined by a single-crystal X-ray diffraction analysis (Fig. 1).[11] Analysis of the *E,E*-dienyl moiety reveals a slightly deviation from the coplanar conformation in the solid-state (C15–C5–C6–C18 dihedral angle=−28.3°).[12]

A mechanistic proposal for the formation of compounds **7** is illustrated in Scheme 2. The process would initiate by Cr(0)-to-Rh(I) carbene ligand transfer leading to the Rh(I) carbene complex **I**.[2,3,7–9,13] Then, a chemo- and regioselective metalla-[4+2]-cycloaddition involving the terminal C═C bond of the allene would

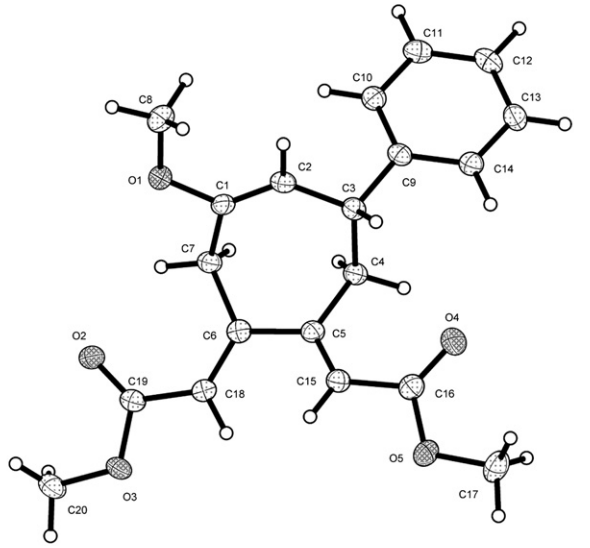
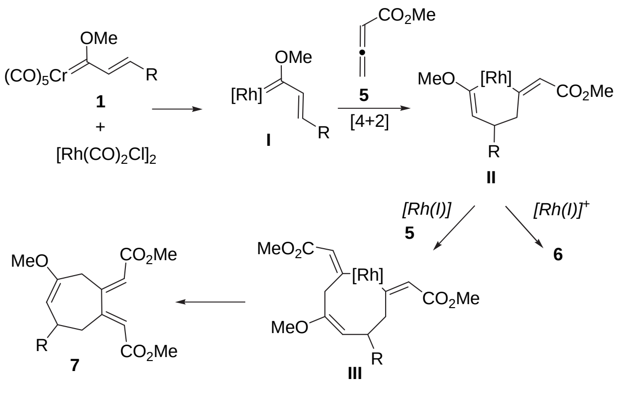


Figure 1. X-ray structure of compound **7b** (ellipsoids at 30% probability level).

lead to the metallacyclohexene species **II**.[8] The participation of intermediate **II** seems reasonable to account for the formation of both cyclopentene **6** and cycloheptene **7** derivatives. Thus, when using a cationic Rh(I)-catalyst, particularly in the presence of the π-acceptor ligand CO, the reductive elimination is favored yielding the cycloadduct **6**.[7,8] Conversely, more electron rich neutral Rh(I)-catalysts retard the reductive elimination allowing for the insertion of a second allene unit. Interestingly, the insertion step takes place regioselectively involving the bond between rhodium and the more nucleophilic sp^2-carbon giving intermediate **III**,[14] which in turn evolves into the cycloadduct **7** by reductive elimination. Probably minimizing the steric repulsion between the ester groups and rhodium ligands (intermediate **III**) is responsible for the observed *E*,*E*-stereochemistry of **7**.



Scheme 2.

In summary, we have discovered a new three-component [3+2+2]-cyclization mode of readily available alkenyl Fischer carbene complexes by reaction with methyl 2,3-butadienoate in the presence of Rh(I) as catalyst. Again, a qualitative modification of the reactivity of group 6 metal carbenes is achieved by metal exchange.[15] In spite of the moderate yield and selectivity, this process allows access to highly functionalized bis-1,2-alkylidene cycloheptenes in an operationally simple process. According to our proposal, the whole process comprises some notable features in terms of selectivity, (i) the [4+2] cycloaddition and Rh/C insertion reactions involve the unactivated allene C=C bond (**II** and **III**; chemoselectivity), rhodium being linked to the central allene carbon (**II** and **III**; regioselectivity), (ii) the insertion of the allene unit occurs into the bond between Rh and the methoxy-substituted carbon (**III**; regioselectivity), (iii) the *E*,*E*-diastereoisomer is exclusively or preferentially formed (**III**, stereoselectivity).

3. Experimental section

All reactions were carried out under N_2 using standard Schlenck techniques. THF, Et_2O, and dioxane were destilled from sodium–benzophenone, DMF were dried using activated MS 4Å, and CH_2Cl_2 and MeCN were destilled from CaH_2. TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator. Flash column chromatography was carried out on silica gel 60 (230–240 mesh). ^1H NMR (300, 400 MHz) and ^{13}C NMR (75, 100 MHz) spectra were measured in $CDCl_3$ at ambient temperature on a Bruker AV-300, DPX-300, AV-400 and AMV-400 instruments, respectively, with tetramethylsilane (δ=0.0 ppm, ^1H NMR), $CDCl_3$ (δ=77.0, ^{13}C NMR) as internal standard. Carbon multiplicities were assigned by DEPT techniques. IR spectra were carried out in a Mattson 3000 FTIR instrument using CCl_4. Elemental analyses were carried out on Perkin–Elmer 2400 and Carlo Erba 1108 microanalyzers. Fischer carbene complexes **1a–g** were prepared from the corresponding alkenyllithium compounds following the general procedure described by Fischer.[16] Methyl 2,3-butadienoate **5** was prepared according to a literature procedure.[17] Rhodium catalysts, except [Rh(cod)(naphthalene)][SbF_6],[18] were commercially available and were used without further purification.

3.1. Representative procedure for Rh(I)-catalyzed [3+2+2]-cyclization of alkenyl Fischer carbene complexes with methyl 2,3-butadienoate 5 (Table 1, entry 7)

To a suspension of alkenyl Fischer carbene complex **1a** (184 mg, 0.50 mmol) and $[Rh(CO)_2Cl]_2$ (19 mg, 0.05 mmol) in dioxane (10 mL), methyl 2,3-butadienoate **5** (147 mg, 1.5 mmol) was added. The resulting mixture was stirred for 16 h at ambient temperature. The solvent was removed under vacuum and the residue was triturated with *n*-pentane/Et_2O (1:1), filtered through a short plug of Celite® and the resulting solution was concentrated under vacuum. The resulting residue was purified by flash column chromatography (SiO_2, hexane/EtOAc, 3:1 v/v) to yield **7a** (99 mg, 53%) as a pale yellow oil.

*3.1.1. (5E,7E)-1-Methoxy-5,7-(di(methoxycarbonyl)methylen)-3-(4-methoxyphenyl)cyclohept-1-ene (**7a**).* ^1H NMR ($CDCl_3$): 2.85 (dd, *J*=13.5, 11.4 Hz, 1H), 3.48 (s, 3H), 3.52–3.84 (m, 12H), 4.29 (d, *J*=17.7 Hz, 1H), 4.62 (d, *J*=4.4 Hz, 1H), 6.00 (br s, 1H), 6.04 (s, 1H), 6.86 (d, *J*=8.5 Hz, 2H), 7.26 (d, *J*=8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): 32.8 (CH_2), 37.2 (CH_2), 42.2 (CH), 51.3 (CH_3), 51.5 (CH_3), 54.7 (CH_3), 55.3 (CH_3), 100.2 (CH), 113.8 (CH), 115.6 (CH), 116.4 (CH), 128.4 (CH), 137.8 (C), 153.6 (C), 157.0 (C), 158.2 (C), 159.0 (C), 166.2 (C), 166.4 (C). IR (NaCl): 3055, 2983, 1712, 1648, 1419, 1263, 736 cm^{-1}. Elemental analysis calcd for $C_{21}H_{24}O_6$: C, 67.73; H, 6.50; found C, 67.91; H, 6.43.

*3.1.2. (5E,7E)-3-Phenyl-1-methoxy-5,7-(di(methoxycarbonyl)methylen)cyclohept-1-ene (**7b**).* The representative procedure was followed using **1b** (168 mg, 0.50 mmol). After 24 h, purification by column chromatography (SiO_2, hexane/EtOAc, 3:1) yielded **7b** (70 mg, 41%) as a pale yellow oil. A slow diffusion of Et_2O in a solution of **7b** in CH_2Cl_2 at -20 °C afforded appropriate crystals for X-ray diffraction studies. ^1H NMR ($CDCl_3$): 2.88 (dd, *J*=13.8, 11.6 Hz, 1H), 3.48 (s, 3H), 3.61 (dd, *J*=13.8, 4.8 Hz, 1H), 3.68 (br s, 1H), 3.73 (s, 3H), 3.75 (s, 3H), 3.82–3.88 (m, 1H), 4.31 (d, *J*=17.7 Hz, 1H), 4.64 (d, *J*=4.6 Hz, 1H), 6.01 (d, *J*=1.9 Hz, 1H), 6.05 (s, 1H), 7.20–7.32 (m, 5H). ^{13}C NMR ($CDCl_3$): 32.7 (CH_2), 37.0 (CH_2), 43.0 (CH), 51.4 (CH_3), 51.5 (CH_3), 54.7 (CH_3), 99.8 (CH), 115.6 (CH), 116.4 (CH), 126.5 (CH), 127.4

(CH), 128.5 (CH), 145.7 (C), 153.7 (C), 156.9 (C), 158.9 (C), 166.2 (C), 166.3 (C). IR (NaCl): 3053, 2987, 1719, 1644, 1421, 1265, 908, 736 cm^{-1}. Elemental analysis calcd for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48; found: C, 70.28; H, 6.53.

*3.1.3. (5E,7E)-3-(4-Chlorophenyl)-1-methoxy-5,7-(di(methoxycarbonyl)methylen)cyclohept-1-ene (**7c**).* The representative procedure was followed using **1c** (185 mg, 0.50 mmol). After 24 h, purification by column chromatography (SiO_2, hexane/EtOAc, 3:1) yielded **7c** (75 mg, 40%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$): 2.92 (dd, *J*=13.7, 11.2 Hz, 1H), 3.52 (s, 3H), 3.61 (dd, *J*=13.7, 5.0 Hz, 1H), 3.74–3.92 (2s+m, 8H), 4.31 (d, *J*=17.6 Hz, 1H), 4.62 (d, *J*=4.6 Hz, 1H), 6.05 (d, *J*=1.9 Hz, 1H), 6.09 (s, 1H), 7.29–7.32 (m, 4H). ^{13}C NMR ($CDCl_3$): 32.7 (CH_2), 36.7 (CH_2), 42.4 (CH), 51.4 (CH_3), 51.5 (CH_3), 54.8 (CH_3), 99.3 (CH), 115.9 (CH), 116.5 (CH), 128.6 (CH), 128.8 (CH), 132.1 (C), 144.0 (C), 154.2 (C), 156.5 (C), 158.5 (C), 166.1 (C), 166.3 (C). IR (NaCl): 3053, 2986, 1704, 1605, 1442, 1167, 895 cm^{-1}. Elemental analysis calcd for $C_{20}H_{21}ClO_5$: C, 63.75; H, 5.62; found: C, 63.59; H, 5.66.

*3.1.4. (5E,7E)-3-Ferrocenyl-1-methoxy-5,7-(di(methoxycarbonyl)methylen)cyclohept-1-ene (**7d**).* The representative procedure was followed using **1d** (223 mg, 0.50 mmol). After 16 h, purification by column chromatography (SiO_2, hexane/EtOAc, 3:1) yielded **7d** (126 mg, 56%) as a pale red viscous oil. ^{1}H NMR ($CDCl_3$): 2.95 (dd, *J*=15.6, 12.5 Hz, 1H), 3.50–3.62 (s+m, 6H), 3.76 (s, 3H), 3.77 (s, 3H), 4.11–4.19 (s+m, 9H), 4.26 (d, *J*=18.0, 1H), 4.85 (d, *J*=4.3 Hz, 1H), 5.98 (br s, 2H). ^{13}C NMR ($CDCl_3$): 33.4 (CH_2), 35.5 (CH), 37.2 (CH_2), 51.3 (CH_3), 51.4 (CH_3), 54.6 (CH_3), 66.7 (CH), 66.8 (CH), 67.2 (CH), 67.5 (CH), 68.5 (CH), 93.9 (C), 100.9 (CH), 115.9 (CH), 116.4 (CH), 153.0 (C), 157.2 (C), 159.5 (C), 166.2 (C), 166.3 (C). IR (NaCl): 3053, 2986, 1713, 1633, 1422, 1265, 1166, 895, 738 cm^{-1}. Elemental analysis calcd for $C_{24}H_{26}FeO_5$: C, 64.01; H, 5.82; found C, 63.95; H, 5.86.

*3.1.5. 3-n-Butyl-1-methoxy-5,7-(di(methoxycarbonyl)methylen) cyclohept-1-ene (**7e**).* The representative procedure was followed using **1e** (159 mg, 0.50 mmol). After 24 h, purification by column chromatography (SiO_2, hexane/EtOAc, 3:1) yielded **7e** (63 mg, 39%, 3:1 mixture of stereoisomers) as a colorless oil. Major isomer: ^{1}H NMR ($CDCl_3$): 0.88–0.94 (m, 3H), 1.32–1.63 (m, 6H), 2.43–2.46 (m, 1H), 2.76–2.84 (m, 1H), 3.06–3.25 (m, 2H), 3.46 (s, 3H), 3.71 (s, 3H), 3.72 (s, 3H), 4.15 (d, *J*=17.8 Hz, 1H), 4.46 (d, *J*=5.2 Hz, 1H), 5.91 (s, 2H). ^{13}C NMR ($CDCl_3$): 14.1 (CH_3), 22.8 (CH_2), 29.2 (CH_2), 33.8 (CH_2), 35.0 (CH), 35.7 (CH_2), 36.9 (CH_2), 51.2 (CH_3), 51.4 (CH_3), 54.5 (CH_3), 101.2 (CH), 115.7 (CH), 116.2 (CH), 153.3 (C), 157.9 (C), 161.1 (C), 166.2 (C), 166.5 (C). Minor isomer (only clearly assignable signals are listed): ^{1}H NMR ($CDCl_3$): 2.62–2.66 (m, 1H), 3.06–3.10 (m, 1H), 3.56 (s, 3H), 3.67 (s, 3H), 4.61 (d, *J*=14.3 Hz, 1H), 5.02 (d, *J*=4.1 Hz, 1H), 5.94 (br s, 1H), 6.27 (s, 1H). ^{13}C NMR ($CDCl_3$): 13.9 (CH_3), 29.4 (CH_2), 33.7 (CH), 37.0 (CH_2), 37.6 (CH_2), 38.6 (CH_2), 50.8 (CH_3), 55.2 (CH_3), 113.6 (CH), 115.4 (CH), 117.0 (CH), 149.7 (C), 153.2 (C), 159.6 (C), 166.9 (C), 167.4 (C). IR (NaCl): 2953, 2930, 2872, 1716, 1634, 1456, 1378, 1195, 1171, 906, 729, 650 cm^{-1}. Elemental analysis calcd for $C_{18}H_{26}O_5$ (mixture of stereoisomers): C, 67.06; H, 8.13; found C, 67.01; H, 8.25.

*3.1.6. 3-tert-Butyl-1-methoxy-5,7-(di(methoxycarbonyl)methylen) cyclohept-1-ene (**7f**).* The representative procedure was followed using **1f** (159 mg, 0.50 mmol). After 24 h, purification by column chromatography (SiO_2, hexane/EtOAc, 4:1) yielded **7f** (76 mg, 47%, 5:1 mixture of stereoisomers) as a colorless oil. Major isomer: ^{1}H NMR ($CDCl_3$): 1.03 (s, 9H), 2.33–2.47 (m, 1H), 2.53 (t, *J*=12.0 Hz, 1H), 3.35–3.44 (m+s, 5H), 3.71 (s, 3H), 3.72 (s, 3H), 4.22 (d, *J*=18 Hz, 1H), 4.55 (d, *J*=5.6 Hz, 1H), 5.91–5.93 (m, 2H). ^{13}C NMR ($CDCl_3$): 27.2 (CH_3), 30.8 (CH_2), 33.2 (CH_2), 34.4 (C), 46.2 (CH), 51.2 (CH_3), 51.4 (CH_3), 54.4 (CH_3), 97.8 (CH), 114.9 (CH), 116.3 (CH), 153.6 (C), 158.6 (C), 161.1 (C), 166.3 (C), 166.4 (C). Minor isomer (only clearly assignable signals are listed): ^{1}H NMR ($CDCl_3$): 1.04 (s, 9H), 2.91 (dd, *J*=17.0, 11.9 Hz, 1H), 3.09–3.17 (m, 1H), 3.10–3.16 (m, 1H), 3.59 (s, 3H), 3.69 (s, 3H), 4.60–4.66 (m, 1H), 5.20 (d, *J*=5.1 Hz, 1H), 5.90 (br s, 1H), 6.28 (d, *J*=2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): 27.8 (CH_3), 33.9 (CH_2), 38.6 (CH_2), 44.1 (CH), 51.1 (CH_3), 55.6 (CH_3), 110.3 (CH), 116.0 (CH), 117.8 (CH). IR (NaCl): 3053, 2966, 2901, 1713, 1633, 1434, 1265, 1167, 895, 740 cm^{-1}. Elemental analysis calcd for $C_{18}H_{26}O_5$ (mixture of stereoisomers): C, 67.06; H, 8.13; found C, 67.21; H, 8.19.

*3.1.7. 3,3-Dimethyl-1-methoxy-5,7-(di(methoxycarbonyl)methylen) cyclohept-1-ene (**7g**).* The representative procedure was followed using **1g** (145 mg, 0.50 mmol). After 24 h, purification by column chromatography (SiO_2, hexane/EtOAc, 3:1) yielded **7g** (45 mg, 31%, 4:1 mixture of stereoisomers) as a colorless oil. Major isomer: ^{1}H NMR ($CDCl_3$): 1.03 (s, 6H), 2.11 (s, 2H), 2.79 (s, 2H), 3.70 (s, 3H), 3.72 (br s, 6H), 5.55 (s, 1H), 6.13 (s, 1H), 6.84 (s, 1H). ^{13}C NMR ($CDCl_3$): 29.4 (CH_3), 38.0 (C), 40.6 (CH_2), 44.5 (CH_2), 51.1 (CH_3), 51.3 (CH_3), 55.4 (CH_3), 96.1 (CH), 109.8 (CH), 116.9 (CH), 158.3 (C), 159.1 (C), 166.7 (C), 167.2 (C), 167.3 (C). Minor isomer (only clearly assignable signals are listed): ^{1}H NMR ($CDCl_3$): 1.09 (s, 6H), 2.17 (s, 2H), 2.97 (s, 2H), 3.55 (s, 3H), 3.60 (s, 3H), 5.30 (s, 1H), 5.52 (s, 1H), 5.79 (s, 1H). ^{13}C NMR ($CDCl_3$): 30.1 (CH_3), 42.1 (CH_2), 45.5 (CH_2), 55.6 (CH_3), 96.4 (CH). IR (NaCl): 2961, 1710, 1621, 1432, 1139, 895, 737 cm^{-1}. Elemental analysis calcd for $C_{16}H_{22}O_5$ (mixture of stereoisomers): C, 65.29; H, 7.53; found C, 65.15; H, 7.66.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.04.130.

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11. Crystallographic data (excluding structure factors) for the compound **7b** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 769135. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: C44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].
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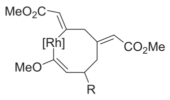

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