Preparation of Donor-Acceptor-Substituted Vinylcyclobutanes

Ursula Gruseck and Manfred Heuschmann*

Institut für Organische Chemie der Universität,
Karlstraße 23, D-8000 München 2

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2-Methylen-1,3-dioxolane (**1**) and the methyl acrylates or crotonates **2** form [2 + 2] cycloadducts **3** which are reduced to give alcohols **6**. Oxidation of these alcohols at low temperatures leads to unstable aldehydes **7**, which either rearrange to dihydropyrans **5** or react with Wittig(-Horner) reagents to afford donor-acceptor-substituted vinylcyclobutanes **8**. The *cis*-vinylcyclobutane **8g** is prepared by [2 + 2] cycloaddition of dioxolane **1** and methyl (2*E*,4*Z*)-hexadienoate (**9**). The configurations and preferred conformations of the vinylcyclobutanes **8** have unequivocally been assigned on the basis of ^{13}C- and ^{1}H-NMR spectra.

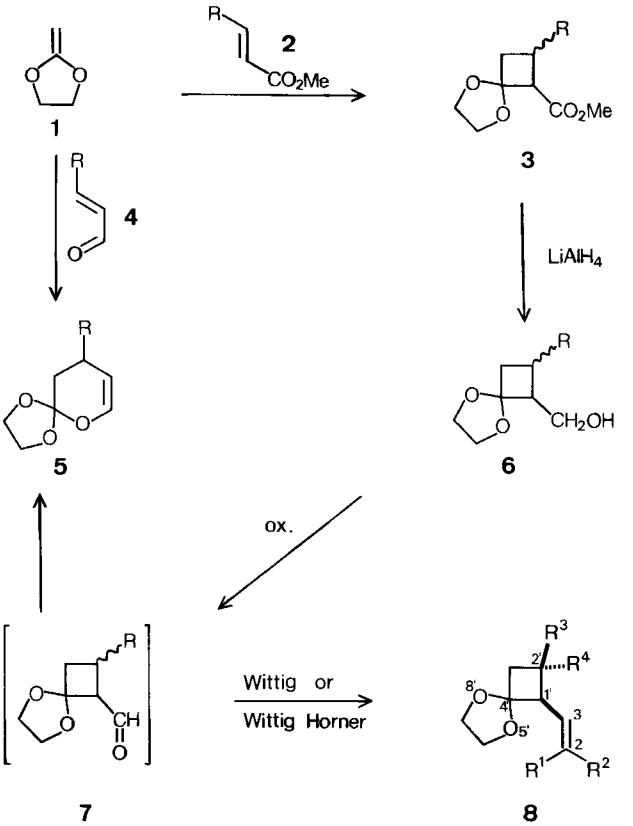
Vinylcyclobutanes are important intermediates in multistep Diels-Alder reactions[1]. The study of the stereospecificity and mechanism of the vinylcyclobutane → cyclohexene rearrangement[2] alone permits a better understanding of the overall process. For a model study, our interest has been focused on the preparation of donor-acceptor-substituted vinylcyclobutanes of type **8**.

The basic framework is easily obtained by a [2 + 2] cycloaddition of 2-methylene-1,3-dioxolane[3] (**1**) to acrylates or crotonates **2**. Whereas cycloaddition to acrylate **2a** occurs in refluxing 2-methyl-2-propanol[4] (the solvent in which **1** is prepared), the purified dioxolane **1** has to be heated with crotonate **2b** in benzene solution in a sealed tube to 165 °C. If 2-methyl-2-propanol is not removed carefully, it adds rapidly to **1** at 165 °C to form an ortho ester like other alcohols do at even lower temperatures[3]. A mixture of the cyclobutanecarboxylates **3b** is isolated in 74% yield with a *cis/trans* ratio of 6:94. The esters **3** are smoothly reduced to the corresponding alcohols **6** with $LiAlH_4$ in THF[4]. The cyclobutanecarboxylates **3b** are converted into the alcohols **6b** in the same *cis/trans* ratio of 6:94.

The structures of the *cis/trans*-substituted cyclobutanes have been assigned on the basis of ^{13}C-NMR spectra as well as chemical reactions (see below). In the ^{13}C-NMR spectrum of 1,2-dimethylcyclobutane, the methyl groups (δ = 5.1) and the adjacent carbon atoms (δ = 7.0) show high-field shifts of the *cis* diastereomer[5]. We have assigned the *cis* structure to the isomers of the esters **3b** and alcohols **6b**, which also exhibit high-field shifts for the methyl groups (δ = 4.4, 5.5) and the cyclobutyl carbon atoms bearing the ester group (δ = 4.3) in **3b** or the hydroxymethyl group (δ = 5.4) in **4b**.

All attempts to isolate the aldehydes **7** after reduction of the esters **3** with diisobutylaluminium hydride[6] or oxidation of the alcohols **6** (PCC[7] with the Sarett-Collins[8], Mukaiyama[9] or Swern reagent[10]) have failed, as compounds **7** rearrange within a few minutes to afford the dihydropyrans **5** at room temperature. Only after rapid workup of the Swern oxidation product of **6b** at low temperatures

Scheme 1



2-7	R
a	H
b	Me

8	R^1	R^2	R^3	R^4
a	H	CO_2Me	H	H
b	CO_2Me	H	H	H
c	Me	CO_2Me	H	H
d	CO_2Me	Me	H	H
e	H	CO_2Me	H	Me
f	CO_2Me	H	H	Me
g	H	CO_2Me	Me	H
h	CO_2Me	H	Me	H
i	Me	CO_2Me	H	Me
k	CO_2Me	Me	H	Me

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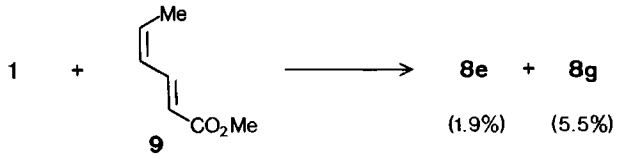
it is possible to obtain a proton NMR spectrum of the aldehyde **7b**, which exhibits a characteristic doublet at δ = 9.62 ($CDCl_3$, J = 2.7 Hz), in a mixture with dihydropyran **5b**. The dihydropyrans **5** are also formed by hetero Diels-Alder reactions[11] of **1** with acrylic or crotonic aldehyde **4a** or **b** at 100°C, possibly via **7** as intermediates. The set of coupling constants obtained from the ^{1}H-NMR spectrum in [D]Chloroform proves that the methyl group of the dihydropyran **5b** strongly prefers the pseudoequatorial position[12]. Comparable rearrangements have been found for related donor-acceptor-substituted cyclobutanes[11b,13].

Table 1. Yields and *E*/*Z* ratios (in parenthesis) of the distilled mixtures and yields of the chromatographically separated *E*/*Z* diastereomers of the vinylcyclobutanes **8** obtained in Wittig or Wittig-Horner reactions

	Wittig			Wittig-Horner		
8	% (E : Z)	%E	%Z	% (E : Z)	%E	%Z
a		49			59	
	69 (78 : 22)			88 (87 : 13)		
b			15			10
c		58			36	
	63 (98 : 2)			54 (73 : 27)		
d						13
e		46			57[a]	
	67 (85 : 15)			83 (78 : 22)		
f			8			14[b]
i		67			18	
	71 (96 : 4)			53 (41 : 59)		
k						25

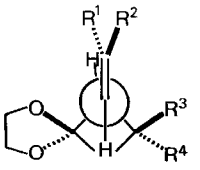
[a] Mixture of 57% **8e** and 1.5% **8g**. — [b] Mixture of 14% **8f** and 1.3% **8h**.

However, following a procedure recently published by Ireland[14], we have succeeded in intercepting the aldehydes **7**, prepared by the method of Swern at −70°C, with a two- or threefold excess of phosphoranes or sodium phosphonates at low temperatures. Slow warming of the mixture to room temperature before aqueous workup leads to the formation of the vinylcyclobutanecarboxylates **8** (Table 1) in acceptable to good yields besides small amounts of the dihydropyrans **5** (4−11%). The formation of **5b** cannot be suppressed totally even with a tenfold excess of Wittig or Wittig-Horner reagents. Only the *trans* isomers **8e**, **f**, **i** and **k** are formed starting from a 6:94 *cis*/*trans* mixture of the alcohol **6b** when phosphorus ylides are used, indicating that the steric hindrance in *cis*-**7b** prevents the Wittig synthesis, whose reaction rate is too slow to compete with the rearrangement to the dihydropyran **5b**. With a twofold excess of sodium phosphonates up to 3% of the *cis*-vinylcyclobutanes **8g** and **h** are also formed. We have not succeeded in separating the diastereomers **8e** or **f** from **8g** or **h**, respectively, but have obtained enriched mixtures of the *cis*-vinylcyclobutanes after two or three consecutive chromatographic separations. The [2 + 2] cycloaddition of the (2*E*,4*Z*)-hexadienoate **9** with the dioxolane **1** finally affords the clean (*cis*,*E*)-vinylcyclobutane **8g**, although in low yield (5.5%). But in this case, the slightly faster moving *trans* diastereomer **8e**, which is also formed in 1.9% yield, can be removed chromatographically without excessive effort.



All vinylcyclobutanes **8** are colorless liquids that may be distilled at 10^{-3} Torr without decomposition. The (*E*/*Z*)-diastereomers are easily separable by chromatography on silica gel with diethyl ether/pentane mixtures and characterized by NMR spectrometry. The mass spectra of the vinylcyclobutanes **8** show one main path of decomposition, namely [2 + 2] cycloreversion, to give the dioxolane **1** (m/z = 86) and dienoates like **9** (m/z = M^+ − 86).

The vicinal coupling constants of the cyclobutyl proton (1′-H) with the vinylic proton (3-H) vary between 8.4 and 10.0 Hz, thus indicating small differences in the conformational equilibria. Couplings of the same order of magnitude have been found for other substituted vinylcyclobutanes[1c], whereas the parent compound shows an average coupling constant of only 6.46 Hz which is interpreted as a slight preference for the *gauche* conformations[15]. If R^1 and/or R^3 of the vinylcyclobutanes **8** are substituents other than hydrogen, the conformations with these coupling protons in antiperiplanar arrangement, which diminishes unfavorable steric interactions, are strongly preferred and lead to coupling constants near 10 Hz. In the two examples with R^1 = R^3 = H, the smaller coupling constants of 8.4 Hz (**1a**) and 8.5 Hz (**1e**) indicate that other conformations have sligthly higher populations in the equilibrium mixture and contribute more to the average coupling constant.



We are indebted to Mr. *H. Schulz* for elemental analyses, to Mr. *H. Huber* for the measurements of ^{13}C-NMR spectra, and Mr. *G. Seidl* for the acquisition of mass spectra.

Experimental

^{1}H NMR: Varian EM 360 and XL 100, Bruker WP 80 and WA 80. — ^{13}C NMR: Varian XL 100 (25.2 MHz), Bruker WP 80 FT (20.2 MHz) und WP 200 (50.3 MHz). — IR: Perkin-Elmer 125 and Bruker IFS 45. — Mass spectra: AEI MS 902. — For preparative chromatography glass plates (20 × 20 cm^{-1}) with 1-mm layers of silica gel $PF_{254+366}$ (Merck) were used. — Benzene and THF

were freshly distilled from sodium hydride, dichloromethane from potassium carbonate, and DMSO and triethylamine from calcium hydride.

5,8-Dioxaspiro[3.4]octane-1-methanol[4] (**6a**), methyl (triphenylphosphoranyliden)ethanoate[16], methyl 2-(triphenylphosphoranyliden)propanoate[16]and methyl 2-(diethoxyphosphinyl)propanoate[17] were prepared according to literature procedures, methyl (dimethoxyphosphinyl)acetate (Aldrich) was used as purchased. 2-Propenal (**4a**) and (2*E*)-butenal (**2b**) were freshly distilled from anhydrous K_2CO_3. Methyl (2*E*,4*Z*)-hexadienoate (**9**) was prepared according to ref.[18] and contained 8% of methyl (2*E*,4*E*)-hexadienoate.

Methyl cis/trans-2-Methyl-5,8-dioxaspiro[3.4]octane-1-carboxylate (**3b**): A solution of 19.2 g (223 mmol) of the dioxolane **1** and 22.3 g (223 mmol) of the crotonate **2b** in 35 ml of dry benzene was heated at 165°C in an alkali-rinsed sealed glass tube for 19 days. The solution was diluted with 100 ml of diethyl ether, washed with 50 ml of aqueous NH_4Cl solution and 50 ml of water, dried with K_2CO_3 and concentrated in vacuo. Distillation at 108–114°C/10^{-3} Torr afforded 30.7 g (74%) of **3b** (*cis*:*trans* = 6:94). – ^{1}H NMR (80 MHz, $CDCl_3$, *trans*-**3b**): δ = 1.14 (d, *J* = 6.0 Hz, 2-Me), 1.7–2.5 (m, 3-H_2), 2.92 (d, *J* = 7.1 Hz, 1-H), 3.61 (s, OMe), 3.85 (m_c, 2 OCH_2). – ^{13}C NMR (20 MHz, $CDCl_3$): *trans*-**3b**: δ = 59.4 (d, C-1), 23.0 (d, C-2), 41.0 (t, C-3), 106.8 (s, C-4), 64.7 (t), 64.8 (t, C-6, C-7), 170.3, (s, C=O), 50.9 (q, OMe), 20.2 (q, 2-Me). – *cis*-**3b**: δ = 55.1 (d, C-1), 23.7 (d, C-2), 41.5 (t, C-3), 107.3 (s, C-4), 64.1 (t), 65.1 (t, C-6, C-7), 170.9 (s, C=O), 51.4 (q, OMe), 16.0 (q, 2-Me). – IR (film): $\tilde{\nu}$ = 1738 cm^{-1} (C=O). – MS (70 eV): *m/z* (%) = 186 (1) [M^+], 155 (7), 144 (15), 113 (21), 86 (100).

cis/trans-2-Methyl-5,8-dioxaspiro[3.4]octane-1-methanol (**6b**): 5.70 g (150 mmol) of $LiAlH_4$ was added in small portions to a solution of 19.5 g (105 mmol) of ester **3b** (*cis*:*trans* = 6:94) in 150 ml of THF. After 18 h of heating at reflux, 6 ml of water, 6 ml of 15% NaOH and another 17 ml of water were added dropwise, and the precipitate was removed by filtration and washed with 200 ml of dichloromethane. After concentration of the solution in vacuo, water was removed azeotropically with benzene, and distillation at 0.01 Torr/130°C yielded 14.0 g (84%) of **6b** (*cis*:*trans* = 6:94). – ^{1}H NMR (80 MHz, $CDCl_3$, *trans*-**6b**): δ = 1.11 (d, *J* = 6.0 Hz, 2-Me), 1.7–2.3 (m, 1-H, 3-H_2), 2.60 (s, OH), 3.34 (m_c, 1-CH_2), 3.80 (m_c, 6-H_2, 7-H_2). – ^{13}C NMR (20 MHz, $CDCl_3$): *trans*-**6b**: δ = 56.3 (d, C-1), 23.1 (d, C-2), 40.9 (t, C-3), 107.6 (s, C-4), 63.9 (t), 64.2 (t, C-6, C-7), 60.5 (t, 1-CH_2OH), 20.6 (q, 2-Me). – *cis*-**6b**: δ = 50.9 (d, C-1), 27.5 (d, C-2, assignment uncertain), 41.2 (t, C-3), 108.3 (s, C-4), 63.5 (t), 64.6 (t, C-6, C-7), 58.6 (t, 1-CH_2OH), 15.1 (q, 2-Me). – IR (film): $\tilde{\nu}$ = 3420 cm^{-1} (OH). – MS (70 eV): *m/z* (%) = 156 (1) [M^+], 116 (26), 99 (17), 86 (100).

Swern Oxidation of Alcohols **6**. – *General Procedure:* To a solution of 1.2*a* mmol of ethanedioyl dichloride in *a* mmol of dichloromethane was added 1.2*a* mmol of DMSO with stirring at –70°C. After 10 min *a* mmol of alcohol **6** and after further 30 min 3*a* mmol of triethylamine were added, and the mixture was stirred at –70°C for 30 min.

2-Methyl-5,8-dioxaspiro[3.4]octane-1-carbaldehyde (**7b**): To a solution of 151 mg (1.20 mmol) of ethanedioyl dichloride in 1 ml of dichloromethane 94 mg (1.20 mmol) of DMSO, after 10 min 158 mg (1.00 mmol) of alcohol **6b** (*cis*:*trans* = 6:94), and after a further 30 min 305 mg (3.00 mmol) of triethylamine were added at –70°C under nitrogen. The mixture was allowed to warm to 0°C within 2.5 h, poured on 10 ml of chilled aqueous ammonium chloride and extracted with 3 × 5 ml of diethyl ether, precooled to 0°C. After 5 min of drying over anhydrous K_2CO_3 at 0°C, the solution was concentrated in vacuo. The ^{1}H-NMR spectrum of the remaining oil showed a mixture of the aldehyde **7b** and the dihydropyran **5b** (50:50). After 5 min at 34°C, 15% of aldehyde **7b** were left, after 30 min only signals of the dihydropyran **5b** were found. – ^{1}H NMR (80 MHz, $CDCl_3$, **7b**): δ = 1.17 (d, *J* = 7.2 Hz, 2-Me), 1.7–3.0 (m, 4 cBu-H), 3.80 (m_c, 2 OCH_2), 9.62 (d, *J* = 2.7 Hz, CH=O).

1,4,6-Trioxaspiro[4.5]dec-7-ene (**5a**): a) The mixture of the Swern oxidation product of 216 mg (1.50 mmol) of the alcohol **3a** was stirred at room temperature for 1 h. After the addition of 5 ml of water the solution was extracted with 3 × 5 ml of diethyl ether. The organic phases were dried over anhydrous K_2CO_3, concentrated in vacuo and distilled at 80–81°C/14 Torr to afford 191 mg (89%) of the dihydropyran **5a** as a colorless oil.

b) A solution of 212 mg (2.46 mmol) of the dioxolane **1** and 140 mg (2.50 mmol) of the aldehyde **4a** in 0.5 ml of benzene was heated at 100°C in an alkali-rinsed sealed glass tube for 19 h. ^{1}H-NMR analysis showed the quantitative formation of the dihydropyran **5a**. Concentration in vacuo and distillation at 81–82°C/16 Torr yielded 318 mg (91%) of **5a**. – ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.7–1.9 (m, 10-H_2), 2.0–2.3 (m, 9-H_2), 4.03 (m_c, 2-H_2, 3-H_2), 4.95 (dt, $J_{7,8}$ = 6.4 Hz, $J_{8,9}$ = 3.4 Hz, 8-H), 6.05 (dt, $J_{7,9}$ = 1.7 Hz, 7-H). – IR (film): $\tilde{\nu}$ = 1735 cm^{-1} (C=C).

9-Methyl-1,4,6-trioxaspiro[4.5]dec-7-ene (**5b**): a) The mixture of the Swern oxidation product of 475 mg (3.00 mmol) of the alcohol **6b** was stirred at room temperature for 1 h. After the additon of 5 ml of water the solution was extracted with 3 × 5 ml of diethyl ether. The organic phases were dried over K_2CO_3, concentrated in vacuo and distilled at 87–88°C/15 Torr to afford 408 mg (87%) of the dihydropyran **5b** as a colorless oil.

b) A solution of 172 mg (2.00 mmol) of dioxolane **1** and 140 mg (2.00 mmol) of the aldehyde **4b** in 0.5 ml of benzene was heated at 100°C in an alkali-rinsed sealed glass tube for 28 h. ^{1}H-NMR analysis showed the quantitative formation of the dihydropyran **5b**. Concentration in vacuo and distillation at 86–88°C/15 Torr yielded 291 mg (93%) of **5b**. – ^{1}H NMR (80 MHz, $CDCl_3$): δ =

Table 2. Conditions of the Wittig and Wittig-Horner reactions to give the vinylcyclobutanes **8** from the aldehydes **7**, prepared in situ from the alcohols **6**

	Reagents (g)					
6	a					Wittig-
	mmol	g	$(COCl)_2$	DMSO	NEt_3	(Horner)
a	9.38	1.35	1.43	0.880	2.85	9.40[a]
	7.00	1.10	1.07	0.656	2.13	3.82[b]
	3.50	0.505	0.533	0.328	1.24	3.66[c]
	1.00	0.144	0.151	0.094	0.304	0.612[d]
b	2.78	0.440	0.424	0.261	0.844	2.64[a]
	3.16	0.500	0.481	0.296	0.958	1.69[b]
	1.00	0.158	0.151	0.094	0.305	1.00[c]
	3.16	0.500	0.481	0.296	0.958	2.09[d]

[a] Ph_3P=$CHCO_2Me$. – [b] $(MeO)_2PO-CH_2CO_2Me$. – [c] Ph_3P=$CMeCO_2Me$. – [d] $(EtO)_2PO-CHMeCO_2Me$.

Table 3. Analytical data of the cyclobutanes **3b**, **6b**, **8** and of the dihydropyrans **5**

	Formula	Mol. mass	C Calcd.	C Found	H Calcd.	H Found
3b	$C_9H_{14}O_4$	(186.2)	58.05	57.86	7.58	7.75
5a	$C_7H_{10}O_3$	(142.2)	59.14	59.14	7.09	7.14
b	$C_8H_{12}O_3$	(158.2)	61.52	61.34	7.74	7.99
6b	$C_8H_{14}O_3$	(158.2)	60.74	61.01	8.92	9.03
8a	$C_{10}H_{14}O_4$	(198.2)	60.59	60.37	7.12	7.12
b	$C_{10}H_{14}O_4$	(198.2)	60.59	60.65	7.12	7.36
c	$C_{11}H_{16}O_4$	(212.2)	62.25	62.20	7.60	7.58
d	$C_{11}H_{16}O_4$	(212.2)	62.25	62.28	7.60	7.19
e	$C_{11}H_{16}O_4$	(212.2)	62.25	62.71	7.60	7.71
f	$C_{11}H_{16}O_4$	(212.2)	62.25	62.56	7.60	7.53
g	$C_{11}H_{16}O_4$	(212.2)	62.25	62.06	7.60	7.58
i	$C_{12}H_{18}O_4$	(226.3)	63.70	63.92	8.02	7.93
k	$C_{12}H_{18}O_4$	(226.3)	63.70	63.60	8.02	7.83

1.07 (d, $J_{9,9\text{-Me}}$ = 7.0 Hz, 9-Mc), 1.70 ($J_{9,10A}$ = 11.1 Hz, $J_{10A,B}$ = 12.8 Hz, 10-H_A), 1.99 ($J_{8,10B}$ = 1.3 Hz, $J_{9,10B}$ = 5.8 Hz, 10-H_B), 2.57 ($J_{7,9}$ = 2.3 Hz, $J_{8,9}$ = 2.3 Hz, 9-H), 4.10 (m_c, 2-H_2, 3-H_2), 4.62 ($J_{7,8}$ = 6.1 Hz, 8-H), 6.12 (7-H). – IR (Film): $\tilde{\nu}$ = 1734 cm^{-1} (C=C).

Wittig Syntheses. – General Procedure: To a solution of 3–3.5*a* mmol of phosphorane in 2*a* ml of dichloromethane at –70°C the cooled solution of the Swern oxidation product was added via canula under argon. The stirred mixture was allowed to warm to room temperature within 10–15 h and poured onto aqueous NH_4Cl. After extraction with 3 × 20 ml of ether and drying over K_2CO_3, the solvent was removed in vacuo and the remaining oil distilled at 10^{-3} Torr/70–100°C bath temperature or chromatographed on silica gel with diethyl ether/pentane (25:75) as eluent. – Concerning the reaction mixture components see Table 2, yields Table 1, analytical and NMR data Tables 3–5.

Wittig-Horner Syntheses. – General Procedure: To a solution of 3*a* mmol of phosphonate in 2*a* ml of THF 3–3.5*a* mmol of sodium hydride was added in portions at 0°C under argon or nitrogen. The mixture was stirred for 30–60 min until no more gas was evolved and cooled to –78°C. The solution of the Swern oxidation product was added via canula, and the mixture allowed to warm to room temperature within 10–15 h and poured onto aqueous NH_4Cl. After extraction with 3 × 20 ml of ether and drying over anhydrous K_2CO_3, the solvent was removed in vacuo and the remaining oil distilled at 10^{-3} Torr/70–100°C bath temperature or chromatographed on silica gel with diethyl ether/pentane (25:75) as eluent. – Concerning the reaction mixture components see Table 2, yields Table 1, analytical and NMR data Tables 3–5.

Methyl (E)-3-(5,8-Dioxaspiro[3.4]oct-1-yl)-2-propenoate (**8a**): IR (film): $\tilde{\nu}$ = 1723, 1653 cm^{-1} (C=O, C=C). – MS (70 eV): *m/z* (%) = 198 (3) [M^+], 170 (19), 139 (17), 112 (8), 86 (100). – R_f = 0.25.

Methyl (Z)-3-(5,8-Dioxaspiro[3.4]oct-1-yl)-2-propenoate (**8b**): IR (film): $\tilde{\nu}$ = 1738 cm^{-1} (C=O). – R_f = 0.33.

Methyl (E)-3-(5,8-Dioxaspiro[3.4]oct-1-yl)-2-methyl-2-propenoate (**8c**): IR (film): $\tilde{\nu}$ = 1734 cm^{-1} (C=O). – MS (20 eV): *m/z* (%) = 212 (21) [M^+], 181 (5), 170 (3), 126 (2), 86 (100). – R_f = 0.28.

Methyl (Z)-3-(5,8-Dioxaspiro[3.4]oct-1-yl)-2-methyl-2-propenoate (**8d**): R_f = 0.36.

Methyl (trans,E)-3-(2-Methyl-5,8-dioxaspiro[3.4]oct-1-yl)-2-propenoate (**8e**): IR (film): $\tilde{\nu}$ = 1724, 1653 cm^{-1} (C=O, C=C). – MS (70 eV): *m/z* (%) = 212 (9) [M^+], 181 (3), 170 (9), 153 (4), 139 (7), 126 (1), 86 (100). – R_f = 0.30.

Table 4. Chemical shifts δ_H (δ values) and selected coupling constants *J* [Hz] of the vinylcyclobutanes **8** in $CDCl_3$ determined from 80-MHz ^{1}H-NMR spectra

	δ								J				
8	2-H	3-H	O-Me	2-Me	1'-H	2'-H, 3'-H	6',7'-H[a]	2'-Me	2,3	2,1'	3,1'	3,2-Me	2',2'-Me
a	5.70	6.88	3.63		3.17	1.5 - 2.4	3.80		15.1	1.3	8.4		
b	5.63	6.33	3.63		3.88	1.6 - 2.4	3.80		11.5	1.2	9.2		
c		6.68	3.65	1.79	3.32	1.5 - 2.4	3.77				9.3	1.4	
d		6.00	3.65	1.89	3.90	1.6 - 2.4	3.75				9.4	1.3	
e	5.67	6.80	3.63		2.64	1.8 - 2.4	3.75	1.13	15.7	1.3	8.6		6.2
f	5.62	6.23	3.62		3.88	1.8 - 2.4	3.75	1.16	11.5	0.8	10.0		5.8
g	5.80	7.04	3.68		3.25	1.9 - 2.5	3.82	1.12	15.5	0.8	10.0		7.0
h[b]	5.90	6.19	3.35		c)	1.8 - 2.6	3.43	0.98	11.5	1.2	9.5		7.2
i		6.70	3.65	1.83	2.84	1.8 - 2.4	3.73	1.14			9.1	1.4	5.6
k		5.95	3.65	1.91	3.52	1.8 - 2.4	3.73	1.12			9.5	1.4	6.0

[a] m_c. – [b] In C_6D_6. – [c] Signal covered by **8f**.

Table 5. Chemical shifts δ_C (δ values) of the vinylcyclobutanes **8** in $CDCl_3$ determined from $^{13}C\{^1H\}$-NMR Spectra (20.15 MHz). All signals show the expected multiplicities in the off-resonance spectra

8	C-1	C-2	C-3	O-Me	2-Me	C-1'	C-2'	C-3'	C-4'	C-6', C-7'		2'-Me
a	166.5	121.4	146.5	51.3		50.8	17.9	33.4	109.8	64.4	64.5	
b	166.0	119.2	147.7	50.9		47.0	19.2	33.3	109.6	64.2	64.5	
c	168.3	127.9	140.0	51.6	13.0	47.2	18.9	33.6	110.0	64.3	64.3	
e	166.8	121.5	145.4	51.4		58.1	27.2	40.9	107.4	64.3	64.5	20.0
f	166.8	119.6	146.3	51.0		53.7	28.7	40.6	107.5	64.1	64.2	20.2
g	166.6	121.5	144.5	51.4		53.2	24.7	40.6	108.3	63.9	64.2	16.4
i	168.5	128.3	139.1	51.7	13.1	54.6	28.4	41.0	107.6	64.4	64.4	20.5

Methyl (trans,Z)-3-(2-Methyl-5,8-dioxaspiro[3.4]oct-1-yl)-2-propenoate (**8f**): IR (film): $\tilde{\nu}$ = 1737, 1650 cm^{-1} (C=O, C=C). – MS (70 eV): *m/z* (%) = 212 (10) [M^+], 181 (4), 170 (9), 153 (8), 139 (7), 126 (3), 86 (100). – R_f = 0.37.

Methyl (cis,E)-3-(2-Methyl-5,8-dioxaspiro[3.4]oct-1-yl)-2-propenoate (**8g**): A solution of 2.35 g (27.3 mmol) of the dioxolane **1** and 1.02 g (8.10 mmol) of the hexadienoate **9** in 5 ml of benzene was heated at 170°C in an alkali-rinsed sealed glass tube for 10 d. The solution was diluted with 20 ml of diethyl ether, extracted with dilute HCl, washed with water, dried over anhydrous K_2CO_3, concentrated in vacuo and distilled at 10^{-3} Torr/110–140°C bath temperature to afford 1.44 g of a colorless oil. This oil was chromatographed twice on silica gel with diethyl ether/pentane (40:60) as eluent to give 95 mg (5.5%, R_f = 0.45) of the vinylcyclobutane **8g** and 32 mg (1.9%, R_f = 0.48) of the vinylcyclobutane **8e**.

Methyl (cis,Z)-3-(2-Methyl-5,8-dioxaspiro[3.4]oct-1-yl)-2-propenoate (**8h**): R_f = 0.38.

Methyl (trans,E)-2-Methyl-3-(2-methyl-5,8-dioxaspiro[3.4]oct-1-yl)-2-propenoate (**8i**): IR (film): $\tilde{\nu}$ = 1734 cm^{-1} (C=O). – MS (70 eV): *m/z* (%) = 226 (2) [M^+], 195 (1), 184 (4), 140 (33), 86 (100). – R_f = 0.32.

Methyl (trans,Z)-2-Methyl-3-(2-methyl-5,8-dioxaspiro[3.4]oct-1-yl)-2-propenoate (**8k**): R_f = 0.38.

CAS Registry Numbers

1: 4362-23-6 / **2b**: 18707-60-3 / (*cis*)-**3b**: 127445-90-3 / (*trans*)-**3b**: 127445-93-6 / **4a**: 107-02-8 / **4b**: 4170-30-3 / **5a**: 127445-86-7 / **5b**: 127445-91-4 / **6a**: 23153-66-4 / (*cis*)-**6b**: 127445-87-8 / (*trans*)-**6b**: 127445-92-5 / **7b**: 127445-88-9 / **8a**: 127445-89-0 / **8b**: 127445-94-7 / **8c**: 127445-95-8 / **8d**: 127445-96-9 / **8e**: 127280-96-0 / **8f**: 127379-37-7 / **8g**: 127379-38-8 / **8h**: 127379-39-9 / **8i**: 127280-97-1 / **8k**: 127379-40-2 / **9**: 30361-31-0 / $(MeO)_2P(O)CH_2CO_2Me$: 5927-18-4 / $Ph_3P{=}CHCO_2Me$: 2605-67-6 / $Ph_3P{=}CMeCO_2Me$: 2605-68-7 / $(EtO)_2P(O)CHMeCO_2Me$: 29668-62-0

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