Vinylcyclobutane-Cyclohexane Rearrangements: Zwitterions as Discrete Intermediates

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Donor-acceptor-substituted vinylcyclobutanes **1** rearrange to cyclohexenes **2** at temperatures between 20 and 195°C. In solvents of low polarity, [2+2] cycloreversion competes with ring enlargement. Under acidic conditions, addition of nucleophiles to vinylcyclobutanes **1** with ring opening is observed. Stereospecificity of rearrangement and [2+2] cycloreversion are functions of temperature, solvent polarity and acid catalysis. Strong dependence on solvent polarity is found for the rates of both reactions. The mechanisms of the thermally induced and acid-catalyzed reactions are discussed on the basis of stereospecificity, kinetic parameters and trapping of intermediates. Two structurally different zwitterions **13** and **14** are proposed as intermediates, one of which is responsible for rearrangement, the other for diastereomerization and [2+2] cycloreversion.

Stereochemistry, energy profiles and mechanism of vinylcyclobutane-cyclohexene rearrangements have been carefully studied by several groups[1,2]. The results of these investigations, however, still leave some doubt, as to whether the rearrangements proceed in a concerted mode or via diradicals as intermediates. Interception of such intermediates would prove their existence under rearrangement conditions and corroborate the two-step mechanism. Stabilized by appropriate substituents, these intermediates are better described as zwitterions instead of diradicals[3] and should react with nucleophiles or electrophiles at their electron deficit or excess sites. For a model study we have chosen donor-acceptor-substituted vinylcyclobutanes **1**.

o = ⊙, ⊕, ⊖
• = ⊙, ⊖, ⊕

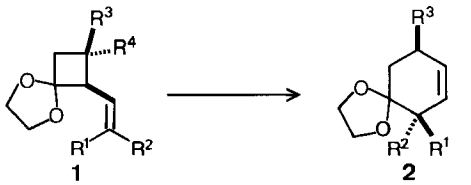
Products

All investigated vinylcyclobutanes **1** decompose on heating in appropriate solvents between 20°C and 210°C. The products identified can be traced back to three types of reactions:

- ring enlargement to give cyclohexenes,
- [2+2] cycloreversion to give dienoates and 2-methylene-1,3-dioxolane,
- addition of nucleophiles to give 3-heptenedioates.

The third reaction is only observed in acidic media. The ratio of ring enlargement to cycloreversion depends on solvent, temperature and structure of the vinylcyclobutanes.

In polar solvents like methanol, *N*-methylformamide, acetonitrile or chloroform, the acrylic ester derivatives **1a**, **b** and **e**–**g** rearrange smoothly to give cyclohexenes **2a**, **c** or **d** on heating (Tables 1 and 4). In apolar solvents like benzene or cyclohexane, these rearrangements are accompanied by



1

1	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

2

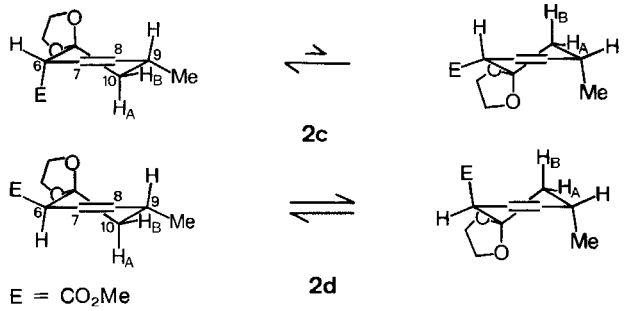
2	R^1	R^2	R^3
a	H	CO_2Me	H
b	Me	CO_2Me	H
c	CO_2Me	H	Me
d	H	CO_2Me	Me
e	CO_2Me	Me	Me
f	Me	CO_2Me	Me

Table 1. Yields[a] of the cyclohexenes **2** obtained in the thermolyses of the vinylcyclobutanes **1a**–**d**

1	Solvent	Temp. (°C)	2 (%)
a	C_6H_6	190	**a** 93
	MeCN	124	96[b]
	MeOH	80	97
	AcOH	80	60[b]
	$HClO_4$/AcOH	20	25
b	C_6H_6	190	84
	AcOH	80	18[b]
c	HCONHMe	162	**b** 32
	$LiClO_4/Et_2O$	84	81
d[c]	$LiClO_4/Et_2O$	84	79[b]

[a] Yields ±2% determined by ^{1}H-NMR standard analysis in sealed tubes. — [b] Isolated yield. — [c] **1c** : **1d** = 44:56.

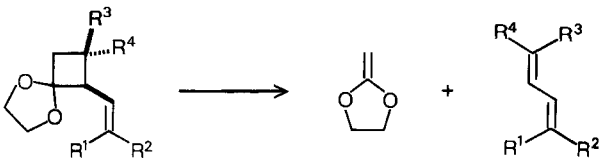
varying amounts of [2+2] cycloreversion, which become more important at higher temperatures. Thus, the yield of cyclohexene **2c** decreases from 75% to 61% when the reaction temperature for the thermolysis of vinylcyclobutane **1e** in benzene is raised from 160°C to 190°C. [2+2] Cycloreversion is the dominant reaction of the methacrylic esters **1c**, **d**, **i** and **k** in most solvents tested. Only in the highly polar mixture of 43% $LiClO_4$ in diethyl ether[4] (wt./wt.) does rearrangement in yields between 79 and 81% occur. In *N*-methylformamide the cyclohexenes **2b** and **e** have been identified as side products in 32 and 37% yield, respectively.



The structures of the cyclohexenes **2** have unambiguously been assigned on the basis of elemental analysis, infrared, mass and NMR spectra. The distinction between the *cis*- and *trans*-cyclohexenes **2c** and **2d** has required a detailed investigation of the high-resolution proton NMR spectra[5a]. All chemical shifts and coupling constants of the nine spin systems of the cyclohexene protons have been evaluated. Independent of the preferred conformation, the *cis*-cyclohexene **2c** always has one pseudoequatorial and one pseudoaxial proton at C-6 and C-9, which should lead to different sets of allylic and vicinal coupling constants with the olefinic protons. In the *trans*-cyclohexene **2d**, however, both the 6- and 9-protons occupy either pseudoaxial or pseudoequatorial positions and should exhibit similar sets of coupling constants. Indeed, the expected behavior is observed. Whereas the 6- and 9-protons of the *trans*-cyclohexene **2d** show similar allylic couplings of −2.44 and −2.47 Hz and vicinal couplings of 2.91 and 2.58 Hz, respectively, the allylic (1.38 and −2.64 Hz) and the vicinal couplings (4.57 and 2.12 Hz) differ considerably in the *cis* diastereomer **2c**. These data point to one strongly preferred half-chair conformation for *cis*-cyclohexene **2c** with the methyl group in pseudoequatorial and the ester group in pseudoaxial position. In the *trans*-cyclohexene **2d** both the methyl and ester groups prefer to occupy pseudoequatorial positions, but the di-pseudoaxial conformer also contributes to the ^{1}H-NMR data. Clear indications of a conformational equilibrium are ^4J coupling constants of both protons 10_A (with 8-H: 0.77 Hz) and 10_B (with 6-H: 0.78 Hz). In the *cis* diastereomer **2c** only one 10-H, the equatorial 10-H_B, is coupled to both 6-H (1.64 Hz) and 8-H (0.97 Hz). This assignment is corroborated by the fact that the homoallylic coupling[5b] $J_{6,9}$ is somewhat smaller in the *cis*- than in the *trans*-cyclohexene with 2.42 and 3.02 Hz, respectively, and by a large coupliung constant J = 10.93 Hz of 9-H with the axial proton 10-H_A. The *trans*-cyclohexene **2d** shows couplings of 5.83 and 8.90 Hz for the vicinal coupling of 9- and 10-protons. In tetrachloromethane these couplings are even smaller with only 5.7 and 7.3 Hz.

Assuming similar conformational preferences for the cyclohexenes **2e** and **f**, which bear an additional methyl group at C-6, *cis* and *trans* assignments have been made on the basis of a smaller set of coupling constants and chemical shifts. The typical differences in the chemical shifts of the cyclohexene carbons of *cis* and *trans* compounds **2c** and **d**, respectively, have also been found for the homologs **2e** and **f** (see Table 13, experimental section). Only the expected deshielding of carbon 10 in **2f** compared to **2e** is offset by the δ-effect of the pseudoaxial 6-methyl group.

Rearrangements in deuterated solvents such as [D_4]methanol or [D_4]acetic acid do not lead to deuterium incorporation into the cyclohexenes **2**.



1 **3** **4**

The substituent key for the dienoates **4** is the same as for the vinylcyclobutanes **1**

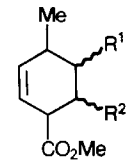
Table 2. Yields[a] of the dienoates **4** obtained in the thermolyses of the vinylcyclobutanes **1a–d**

1	Solvent	Temp. (°C)	4 (%)
a	cC_6H_{12}	200	8
	C_6H_6	190	6
b	cC_6H_{12}	202	21
	C_6H_6	190	16
c	MeCN	165	87[b,c]
	HCONHMe	162	66[d]
	$LiClO_4/Et_2O$	84	6[d]
d	$LiClO_4/Et_2O$	84	8[d]

[a] Yields determined by ^{1}H-NMR standard analysis in sealed tubes. — [b] Isolated yields. — [c] ≥95% **4c**. — [d] ≥90% **4c**.

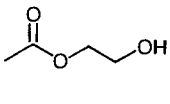
In apolar solvents and at higher temperatures [2+2] cycloreversions compete with rearrangement of the acrylic esters **1a**, **b** and **1e–h**. For the methacrylic esters **1c**, **d**, **i** and **k** this is the only reaction observed in all apolar and most polar solvents (Table 2). The dienoates **4** and their respective geometries are easily identified by means of NMR spectra and a comparison with authentic samples. The pentadienoates **4a** and **b** are not stable under the reaction conditions and form the known dimers and polymers[6]. Depending on temperature and concentration, a small part of the dienoates **4e–h** also dimerizes to give diastereomeric mixtures of the Diels-Alder adducts **5**[7]. We have not tried

to separate these dimers and to determine their configurations. In our analysis we have simply added the amount of dimers to the yield of monomers.



5	R^1	R^2
	CH=CHMe	CO_2Me
	Me	$CH=CHCO_2Me$
	$CH=CHCO_2Me$	Me
	CO_2Me	CH=CHMe

5



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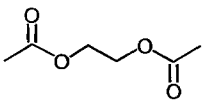

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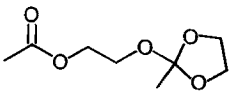

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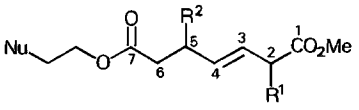
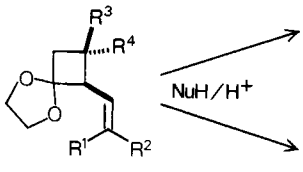
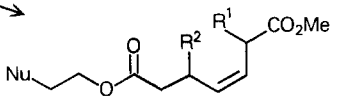
We have not been able to identify unequivocally the second fragment of the [2+2] cycloreversion processes, e.g. 2-methylene-1,3-dioxolane (**3**): **3** polymerizes very readily[8], part of it probably decomposes under the reaction conditions, for example at 195°C in benzene, to unknown compounds as we have found independently for pure **3** in benzene at 200°C. However, after treatment of the reaction mixtures with water, we have identified 2-hydroxyethyl acetate (**6**) in 70–80% of the expected yield. Acetate **6** is formed quantitatively from methylene-dioxolane **3** and water[8]. If the thermolyses are performed in solvents which had not been dried carefully, acetate **6** is identified in the reaction mixture along with varying amounts of the diacetate **7** and ortho ester **8**, which has been isolated in the thermolysis mixture of **1c** in acetonitrile in 81% yield.



9, 11



1



10, 12

	Nu
9, 10	OH
11, 12	OAc

9, 10, 11, 12	R^1	R^2
a	H	H
b	Me	H
c	H	Me
d	Me	Me
e	Me	Me

In acidic media, water or acetic acid add to the vinylcyclobutanes **1** to afford the heptenedioates **9**–**12**. The formation of alcohols **9** and **10** is due to small amounts of water in the solvents and can be suppressed by careful drying. They are not formed without acid catalysis. The acidity of 1,1,1,3,3,3-hexafluoro-2-propanol (HFP, pK_A = 9.37[9]) is sufficient to catalyze the addition of water impurities, but in aqueous methanol no addition products have been found. The thermolyses of vinylcyclobutanes **1** in glacial acetic acid afford only the (*E*)-heptenedioates **9** and **11**, the (*Z*) diastereomers **10** and **12** arise from the perchloric acid catalyzed reaction. While these ring-opened adducts have been found as side products of ring enlargement with the acrylic esters **1a**, **b**, **e** and **f**, they are the only detected and isolated products from the methacrylic esters **1c**, **d**, **i** and **k** (Table 3). If *O*-deuterated acids are used, deuterium is incorporated exclusively into the 2-position.

Table 3. Yields[a] of 3-heptenedioates **9**, **10**, **11** and **12** obtained in the thermolyses of the vinylcyclobutanes **1** in acidic media

1	Solvent	Acid	Temp. (°C)	9 (%)	10 (%)	11 (%)	12 (%)
a	AcOH		80			31	
	AcOH[c]		80	35[b]			
	AcOH	$HClO_4$	20			26	49
b	AcOH[c]		80	24		44	
	AcOH		80			88[b]	
c	AcOH[c]		80	60[b]		33[b]	
	AcOH	$HClO_4$	20			95[b]	
e	HFP[c,f]		22	13[b]	17[b]		
	AcOH		80			15	
	AcOH	$HClO_4$	20			36	59
	MeCN[c]	$SnCl_4$	0	40[b]	33[b]		
f	AcOH		80			73[b]	
	AcOH[c]		80	73[b]			
i	AcOH		120			92[b,d]	
	AcOH	$HClO_4$	25			96[d]	
	MeCN[c]	$SnCl_4$	20	80[b,e]			

[a] Yields ±3% determined by ^{1}H-NMR standard analysis. – [b] Isolated yields. – [c] Containing water. – [d] 50:50 diastereomeric mixture. – [e] 60:40 diastereomeric mixture. – [f] 1,1,1,3,3,3-Hexafluoro-2-propanol. – [g] **9c**:**10c** = 42:58.

On the basis of the ^{13}C-NMR spectra an unequivocal determination of the structures of the (*E*/*Z*) diastereomers **11** and **12** has been achieved. The (*Z*) geometries have been assigned to the heptenedioates **12a** and **c** on the basis of high-field shifts in the ^{13}C-NMR spectra for C-2 (5.0; 4.9) and C-5 (4.9; 4.2) in comparison with **11a** and **c**. The diastereomers **9d** and **e** or **11d** and **e** are also easily distinguished, due to their different sets of ^{13}C-NMR data. Assignment of their configurations, however, on the basis of the available findings is not possible. The interrelations between acetoxy derivatives **11** or **12** and alcohols **9** or **10** have been shown by the smooth and quantitative conversion of **9** into **11** or **10** into **12** with acetyl chloride in [*D*]chloroform at room temperature.

A mixture of (*E,Z*)-heptenedioates **11c** and **12c** is also formed by treatment of the cyclohexene **2c** with perchloric acid in glacial acetic acid. However, this ring opening of the cyclohexene is much slower than that of the vinylcyclobutanes and can only account for a very small part of the produced heptenedioates.

The rearrangement of the vinylcyclobutanes **1** is catalyzed by all kinds of Brønsted and Lewis acids like formic acid, trifluoroacetic acid, sulfuric acid, zinc iodide, ferric trichloride, tin tetrachloride or titanium tetrachloride. The carboxylic acids are also converted into side products analogous to the triesters **11** and **12** in the same ratio of approximately 35:65. However, these triesters have not been isolated, and the structure assignment is based on their ^{1}H-NMR spectra only.

Stereospecificity[10]

Of the racemic vinylcyclobutanes **1** used, only those with at least two stereogenic centers can be employed for stereospecificity studies of the ring enlargement reaction. (*E/Z*) diastereomerism of **1** alone is not sufficient. Thus, of the diastereomeric vinylcyclobutanes **1a** and **b** or **1c** and **d**, each pair affords the same cyclohexene, **2a** or **2b**, respectively. The vinylcyclobutanes **1e–k**, however, give rise to cyclohexenes **2c–f** with two stereogenic centers, and the configuration (*cis* or *trans*) allows to determine the stereospecificity and thus to draw conclusions about the steric course of the rearrangement.

Table 4. Yields and diastereomeric ratios[a] of the cyclohexenes **2c–f** obtained from the vinylcyclobutanes **1e–k**

1	Solvent	Temp. (°C)	2 (%)	cis[b] : trans
e	C_6D_6	190	61	100 : 0
		180	65	100 : 0
		170	70	100 : 0
		160	75	100 : 0
	$CDCl_3$	124	95	100 : 0
	MeCN	118	98	100 : 0
	HCONHMe	115	87	100 : 0
	MeOH	100	96[c]	100 : 0
	AcOH	80	85	100 : 0
	$LiClO_4/Et_2O$	70	83	100 : 0
	HFP[d]	22	65[c]	68 : 32
	$SnCl_4$/MeCN	20[e]	87[c]	49 : 51
f	C_6D_6	195	19	41 : 59
		180	22	40 : 60
		170	25	38 : 62
	MeCN	144	75	45 : 55
	MeOH	100	91[c]	69 : 31
	$LiClO_4/Et_2O$	70	78[c]	100 : 0
g	C_6D_6	190	11	24 : 76
	MeCN	144	92	70 : 30
	MeOH	101	95	75 : 25
i	HCONHMe	145	37	e)
	$LiClO_4/Et_2O$	96	74[c]	93 : 7
f)	$SnCl_4$/MeCN	93	78[c]	33 : 67
k[g]	$LiClO_4/Et_2O$	96	78	84 : 16

[a] Yields and ratios ±2% determined by ^{1}H-NMR standard analysis in sealed tubes. – [b] **2c**:**d** or **2e**:**f**. – [c] Isolated yields. – [d] 1,1,1,3,3,3-Hexafluoro-2-propanol. – [e] Only **2e** was identified. – [f] **1i**:**k** = 65:35. – [g] **1i**:**k** = 15:85.

The (*E,trans*) derivative **1e** is converted cleanly into the *cis*-cyclohexene **2c** in all solvents tested with the exception of 1,1,1,3,3,3-hexafluoro-2-propanol (Table 4). No *trans*-cyclohexene **2d** has been found within the limits of detection, which vary from 0.2 to 2%. The (*Z,trans*)-vinylcyclobutane **1f**, however, is usually transformed into mixtures of cyclohexenes **2c** and **d**, the ratio depending on solvent polarity and to a lesser degree on temperature. More polar solvents and higher temperatures favor the formation of the *cis*-cyclohexene **2c**. In the polar mixture of 43% $LiClO_4$ in diethyl ether[4], **2c** was the only product found. Rearrangement of the third diastereomer, (*E,cis*)-vinylcyclobutane **1g**, also leads to a mixture of *cis/trans*-cyclohexenes **2c** and **d**. Again, more polar solvents favor the *cis*-cyclohexene **2c**. In methanol or acetonitrile we have observed mainly rearrangement of all three diastereomers **1e–g**. In benzene or cyclohexane, however, a minor part of **1e** and major parts of **1f** and **g** are lost due to the competing [2+2] cycloreversion. In the case of the (*Z,cis*)-vinylcyclobutane **1h**, which we have only thermolyzed in a mixture together with **1f**, we have not been able to decide whether rearrangement has occurred at all. Within the limits of detection, all of the starting compound seems to undergo [2+2] cycloreversion in benzene between 170 and 195°C.

The cyclohexenes **2c** and **d** are stable under rearrangement conditions even on prolonged heating, ruling out the possibility of *cis/trans*-isomerization *after* the rearrangement. This was shown for *cis*-cyclohexene **2c** in benzene at

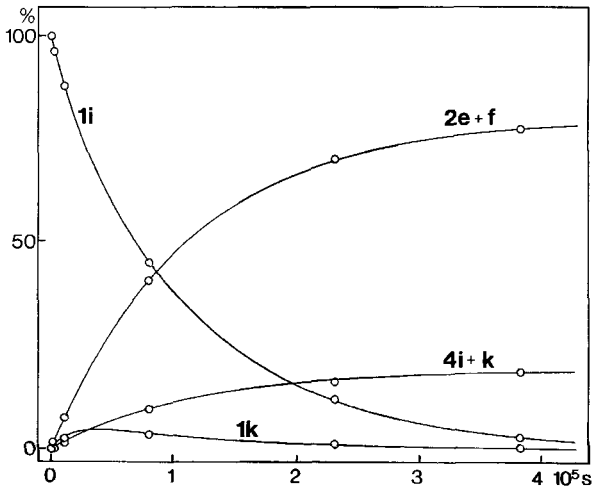


Figure 1. Calculated (—) and observed (○) concentrations of the vinylcyclobutanes **1i** and **k**, cyclohexenes (**2e+f**) and dienoates (**4i+k**) during the thermolysis of vinylcyclobutane **1i** in $LiClO_4$/diethyl ether

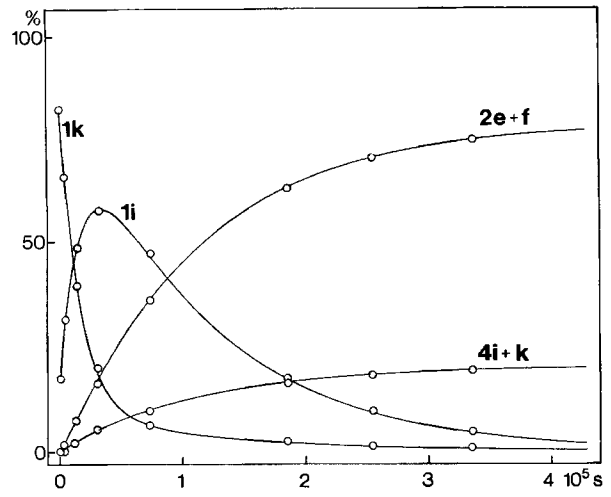


Figure 2. Calculated (—) and observed (○) concentrations of the vinylcyclobutanes **1i** and **k**, cyclohexenes (**2e+f**) and dienoates (**4i+k**) during the thermolysis of the vinylcyclobutanes **1i:k** = 17.6:82.4 in $LiClO_4$/diethyl ether

175°C or in acetonitrile at 165°C and for *trans*-cyclohexene **2d** in benzene at 170°C or methanol at 100°C. Isomerization of the vinylcyclobutanes **1f** and **g** to **1e** *prior* to rearrangement could neither be proved unequivocally nor ruled out, as **1e** reacts much faster than the other diastereomers (vide infra).

The two methacrylic derivatives **1i** and **k** are transformed into cyclohexenes in resonable yields only in $LiClO_4$/diethyl ether at temperatures between 80 and 100°C. Both diastereomers are converted into mixtures of *cis*- and *trans*-cyclohexenes **2e** and **2f**, in which the *cis* diastereomer **2e** dominates. In this case, however, the course of the rearrangement can easily be followed by monitoring the ^{1}H-NMR spectra. The (*Z*)-vinylcyclobutane **1k** first rapidly diastereomerizes to the (*E*)-vinylcyclobutane **1i** until an equilibrium of **1i:k** $\approx$ 9:1 is reached. Starting with pure (*E*)-vinylcyclobutane **1i** the same equilibrium mixture is formed. In a markedly slower reaction, rearrangement to the cyclohexenes **2e** and **f** competes with (*E*/*Z*) diastereomerization (Figures 1 and 2). It is possible to simulate the kinetic system by assuming that the rerrangement of (*E*)-vinylcyclobutanes **1i** to *cis*-cyclohexene **2e** and of (*Z*)-vinylcyclobutane **1k** to *trans*-cyclohexene **2f** occurs totally stereospecifically. For the vinylcyclobutanes **1c** and **d** diastereomerization yielding a 86:14 mixture is also faster than rearrangement, but here it has no bearing on the products.

A (*Z*/*E*) or *cis*/*trans* diastereomerization of vinylcyclobutanes **1f** or **g** to the (*E*,*trans*) isomer **1e** may be responsible for the lack in stereospecificity in the rearrangements of **1f** and **g**, too. In these cases, however, one can calculate easily by mcans of rate constants (see next chapter) that only very small amounts of **1e** (with concentration maxima of 3% of the starting materials or less) are formed. Indeed, we detected the intermediate formation of 1–2% of diastereomer **1e** during the thermolyses of the vinylcyclobutanes **1f** and **g** in [D_6]benzene. However, due to the limits of our analytical method we have not been able to decide whether *all* of *cis*-cyclohexene **2c** is formed via (*Z*/*E*) or *cis*/*trans* diastereomerization prior to rearrangement.

As a conclusion we state that these vinylcyclobutane-cyclohexene rearrangements are not stereospecific with regard to starting compounds but stereoselective with regard to products in highly polar media. Loss in stereospecificity can be traced back to diastereomerization of the starting compounds in some cases. The actual rearrangement step may well proceed with a high degree of stereospecificity in all cases.

Thermally induced and acid-catalyzed rearrangements show different selectivities. The (*E*)-vinylcyclobutane **1e** rearranges to a 49:51 mixture of cyclohexenes **2c** and **d** in the presence of tin tetrachloride. Likewise, the tin tetrachloride catalyzed rearrangement of vinylcyclobutanes **1i** and **k** yields *cis* and *trans*-cyclohexenes in a ratio of **2e:f** = 34:66. This is preparatively the best access to the *trans*-cyclohexenes **2d** and **f**.

Stereospecificity is clearly different for rearrangement and [2+2] cycloreversion. The methacrylic ester **1c** is converted only into the (2*E*)-pentadienoate **4c** in acetonitrile at 165°C with a purity higher than 95%. Thermolyses of the acrylic ester derivatives **1e–h** in benzene are best suited for the investigation, because all possible diastereomers are available and have yielded the four hexadienoates **4e–h**. Stereospecificity of the [2+2] cycloreversion can be determined for two bonds, e.g. the already existing double bond, which becomes bond 2 in the hexadienoates **4**, and the newly formed double bond 4, which corresponds to the former cyclobutane bond. Two minor problems impair the accuracy of the results. The dienoates dimerize to Diels-Alder adducts and diastereomerize under the conditions employed. In our analysis we have simply added the amount of dimers to the yield of monomers, leaving the diastereomeric ratio of the dienoates **4** unchanged. Although this procedure clearly includes an error in the determination of this ratio, it seems justified due to the fact that only small amounts, namely less than 10% of the total yield of dienoates **4**, are concerned and that the ratio usually remains constant throughout the thermolysis within the limits of the ^{1}H-NMR method. In a few critical cases at 190 and 195°C we have used ratios which have been determined after only 35–40% turnover. [2+2] Cycloadditions or Diels-Alder reactions of 2-methylenedioxolane **3** and hexadienoates **4e–h** are too slow to affect their ratio[11]. Likewise, diastereomerization of the products is only of minor importance. Under conditions harsher than those applied for the thermolyses, e.g. after heating a clean sample of (2*E*,4*E*)-hexadienoate **4e** in benzene to 200°C for ten hours, we have found only 2% of the (2*Z*,4*E*) diastereomer **4f**. Under the same conditions, 4% of **4f** and 2% of the (2*E*,4*Z*)-hexadienoate **4g** diastereomerize to **4e**. Thus, the stereospecificities given in Table 5 are more likely to be lower limits than the exact numbers. The deviations, however, cannot be more than 2 or 3%.

In [D_6]benzene, hexadienoates **4e**, **f** and **g** are formed from the (*E*,*trans*)-vinylcyclobutane **1e** in yields of 25–39%

Table 5. Yields and ratios[a] of the dienoates **4e–h** obtained from the vinylcyclohexenes **2e–h** in C_6D_6

1	Temp. (°C)	4 (%)	e 2E4E	f 2Z4E	g 2E4Z	h 2Z4Z	Stereospec. b)	c)
e	190	39	90	3	7		93	97
	180	35	95	2	3		97	98
	170	30	98		2		98	100
	160	25	100				100	100
f	195	81	18	74	5	3	92	77
	180	78	19	76	4	1	95	77
	170	75	19	78	3		97	78
g	190	89	5	7	88		88	93
h[d]	195	100			25	75	100	75
	180	100			25	75	100	75
	170	100			20	80	100	80

[a] Yields ±2% and ratios ±3% were determined by ^{1}H-NMR standard analysis in sealed tubes. – [b] Stereospecificity with regard to the former cyclobutane bond. – [c] Conservation of double-bond geometry of **1**. – [d] Yields ±10% and ratios ±10% were calculated from the thermolysis of a mixture containing 83.5% of **1f** and 16.5% of **1h** by comparison with the thermolysis of pure **1f**.

at temperatures between 160 and 190°C. 90–100% of this material exhibits (2*E*,4*E*) geometry, while 0–7% consists of the (2*E*,4*Z*)-hexadienoate **4g** and up to 3% of the (2*Z*,4*E*)-hexadienoate **4f**. No (2*Z*,4*Z*)-hexadienoate **4g** has been detected. The thermolysis of the (*Z*,*trans*)-vinylcyclobutane **1f** at temperatures between 170 and 195°C yields 75–81% of hexadienoates in [D_6]benzene. These products are less homogeneous, consisting of 18–19% **4e**, 74–78% **4f**, 3–5% **4g** and 0–3% **4h**. Rearrangement of the (*E*,*cis*)-vinylcyclobutane **1g** affords 5% **4e**, 7% **4f** and 88% **4g** in a total yield of 89% at 190°C in [D_6]benzene. The results of the thermolyses of (*Z*,*cis*)-vinylcyclobutane **1h** are not as reliable as the others. They have been obtained from a mixture of **1f** and **h** (83:17), and the calculated yields have an accuracy of only ±10%. Despite this uncertainty, the product with retention of stereochemistry, **4h**, is again clearly the dominant one with a yield of 75–80%.

The application of higher temperatures always leads to higher yields of dienoates **4** and lower stereospecificity in the same solvent. The ratios of hexadienoates **4e–h** obviously represent no equilibrium mixtures. Under all conditions examined we have found that the stereochemistry of the acrylic double bond is preserved by more than 75% during the [2+2] cycloreversion process and that the other double bond is formed with a stereospecificity of more than 88% (Table 5).

The methacrylic derivatives **1i** and **k** are converted into almost the same mixture of diastereomeric (*E*/*Z*)-hexadienoates **4i** and **k** (82:18 and 84:16) in 43% $LiClO_4$ in diethyl ether. Still, the stereospecificity may be high, because fast diastereomerization to afford an equilibrium mixture of **1i**:**k** ≈ 9:1 precedes the [2+2] cycloreversion.

Kinetics

In our preparative experiments we had already observed qualitatively that the reaction rates for the rearrangement and also for the [2+2] cycloreversion depend strongly on solvent polarity. To get more reliable quantitative results, we have determined rate constants by monitoring the disappearance of cyclobutanes **1** by means of standard ^{1}H-NMR analysis in sealed tubes. Initially, we have had problems with reproducibility. Sometimes, the rearrangements are accelerated, apparently by impurities in the vinylcyclobutanes **1**, in benzene as well as in $LiClO_4$/diethyl ether,

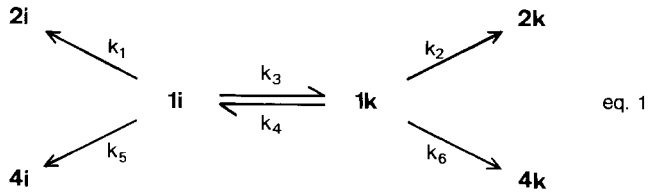
Table 6. First-order rate constants k_T for the decrease of the concentration of the vinylcyclobutanes **1e–h**, k_R for rearrangement and k_C for [2+2] cycloreversion in different solvents

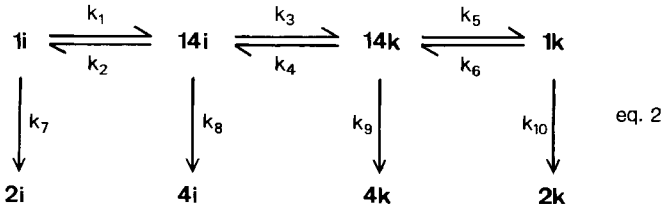
1	Solvent	Temp. (±0.1°C)	$10^5 k_T$ (s^{-1})	$10^5 k_R$ (s^{-1})	$10^5 k_C$ (s^{-1})
e	C_6D_6	189.7	12.0±0.2	7.38	4.62
		179.8	5.74±0.09	3.72	2.02
		170.8	3.23±0.08	2.26	0.97
		160.2	1.36±0.03	1.02	0.34
	MeCN	139.4	41.9±0.8	41.9	
		133.4[a]	27.0±0.3	27.0	
		125.5	14.7±0.2	14.7	
		118.1[a]	9.22±0.22	9.22	
		99.3[b]	2.29±0.02	2.29	
	MeOH	99.5[a]	73.8±1.6	73.8	
		90.0	54.5±0.7	54.5	
		79.9	30.8±0.4	30.8	
		70.0	11.6±0.2	11.6	
		60.0	5.29±0.19	5.29	
f	C_6D_6	195.0[a]	10.3±0.3	1.98	8.30
		180.0	3.20±0.06	0.72	2.48
		170.2[b]	1.42±0.02	0.35	1.07
	MeCN	144.0	4.80±0.16	3.60	1.20
	MeOH	99.7[b]	4.57±0.05	4.57	
g	C_6D_6	189.6	2.24±0.03	0.26	1.98
	MeCN	144.4[b]	12.6±0.3	11.3	1.26
	MeOH	101.0[b]	26.3±0.8	26.3	
h	C_6D_6	195.0[b]	6.28±0.20		6.28
		180.0	2.10±0.07		2.10
		170.2[a]	0.91±0.04		0.91

[a] ±0.3 C – [b] ±0.2 C

lowering the activation energies by as much as 25 kJ mol^{-1} without loss in stereoselectivity for **1e**. These impurities are not yet identified. However, if the vinylcyclobutanes are purified by chromatography *and* distillation in vacuo, reproducible rate constants with deviations of less than 5% result.

As the ratio of rearrangement to [2+2] cycloreversion remains constant throughout the thermolysis of vinylcyclobutanes **1e–g**, the first-order rate constants for each reaction can easily be calculated from the total rate constant and product ratios (Table 6). Evaluation of the rate constants for the methacrylic cyclobutanes **1i** and **k** in $LiClO_4$/diethyl ether is more complicated, because diastereomerization of the vinylcyclobutanes competes successfully with rearrangement and [2+2] cycloreversion. We have solved this problem by means of computer simulation, using the two sets of rate constants formulated in equations 1 and 2.





In the simpler kinetic system of equation 1, which presumes 100% stereospecificity in rearrangement and [2+2] cycloreversion, satisfactory solutions with standard deviations $\sigma = 0.33\%$ and $\sigma = 0.52\%$ have been found for both runs, the one starting with (*E*)-vinylcyclobutane **1i**, the other with a mixture of (*E*/*Z*) diastereomers **1i**:**k** = 17.6:82.4. The calculated rate constants of both runs coincide well having only small deviations due to experimental errors with one exception, namely k_6. A common set of rate constants for both runs also reproduces satisfactorily the experimental values with standard deviations of only 0.33% and 0.49%. The ratio of (2*E*,4*E*)- and (2*Z*,4*E*)-hexadienoates **4i** and **k**, however, are not reproduced satisfactorily, the deviations are clearly outside the experimental errors (Table 8). The second kinetic system of equation 2, which presumes that **14i** and **k** are shortlived intermediates for both diastereomerization and [2+2] cycloreversion, is superior to the simple kinetic system of equation 1 and accounts for all experimental results. The possible nature of the intermediates **14** will be discussed later. It is not necessary to include intermediates for the formation of cyclohexenes **2e** and **f**. Unfortunately, it is only possible to determine the *cis*/*trans* ratio of the cyclohexenes **2e**:**f** in the crude product mixture but not during the course of the reaction. However, the workup of a thermolysis mixture of the (*Z*)-vinylcyclobutane **1k** after only 13% cyclohexene formation shows a *cis*/*trans* ratio **2e**:**f** = 54:46, well away from the ratio after total conversion (82:18) but consistent with the stereospecific rearrangement assumed in equation 2.

The absolute values of the calculated rate constants $k_2 - k_5$, k_8 and k_9 have no significance. Correct solutions with the same standard deviations can be found for unlimited other combinations of these rate constants. However, they must comply with the following conditions:

$$1)\ k_2, k_5 \gg k_1, k_6$$

$$2)\ k_4 : k_9 \geq 100$$

$$3)\ k_3 : k_8 \geq 20$$

Condition 1 prevents that noticeable amounts of intermediates are enriched. Conditions 2 and 3 are necessary to ensure the correct ratios of hexadienoates in both runs. Comparable results have been found for the combined kinetic systems of vinylcyclobutanes **1e–h**. In these cases, however, calculations reveal that the diastereomeric vinylcyclobutanes are formed with maximum concentrations of less than 4% of the starting materials, i.e. in the order of magnitude of the experimental error. Thus, conclusions have to be drawn very carefully. In all cases investigated, kinetics

Table 7. Rate constants determined for the thermolyses of the vinylcyclobutanes **1i** (run 1) or **1i**:**k** = 17.4:82.6 (run 2), and for both runs combined according to equations 1 and 2

	Equation 1		
	Run 1	Run 2	Comb.
$10^6\ k_1$	7.26	7.06	7.21
$10^6\ k_2$	6.00	5.60	5.85
$10^6\ k_3$	4.66	5.17	4.95
$10^5\ k_4$	4.38	5.08	5.05
$10^6\ k_5$	1.58	1.80	1.70
$10^6\ k_6$	3.56	1.65	2.20

	Equation 2		
	Run 1	Run 2	Comb.
$10^5\ k_1$	5.60	5.60	5.60
$10^2\ k_2$	6.75	6.85	6.80
$10\ k_3$	1.20	1.20	1.20
$10\ k_4$	5.30	5.35	5.32
$10^2\ k_5$	3.55	3.65	3.60
$10^5\ k_6$	6.30	6.40	6.35
$10^6\ k_7$	7.31	7.11	7.21
$10^3\ k_8$	2.06	1.99	2.02
$10^3\ k_9$	1.76	1.81	1.80
$10^6\ k_{10}$	5.70	5.50	5.60

Table 8. Experimental and calculated diastereomeric ratios of the cyclohexenes **2e/f** and hexadienoates **4i/k** obtained in the thermolyses of the vinylcyclobutanes **1i** (run 1) or **1i:k** = 17.4:82.6 (run 2), and standard deviations σ of the calculated concentrations optimized for either run and both runs combined according to equations 1 and 2

Run 1			(%)
Exp.	93 : 7	84 : 16	
Eq. 1	93.4 : 6.6	83.6 : 16.4	0.33
Comb.	93.6 : 6.4	90.2 : 9.8	0.33
Eq. 2	93.4 : 6.6	83.9 : 16.1	0.32
Comb.	93.3 : 6.7	83.4 : 16.6	0.39
Run 2			
Exp.	84 : 16	82 : 18	
Eq. 1	83.9 : 16.1	81.8 : 18.2	0.52
Comb.	83.8 : 16.2	76.4 : 23.6	0.49
Eq. 2	84.3 : 15.7	82.2 : 17.8	0.49
Comb.	84.1 : 15.9	82.3 : 17.7	0.51

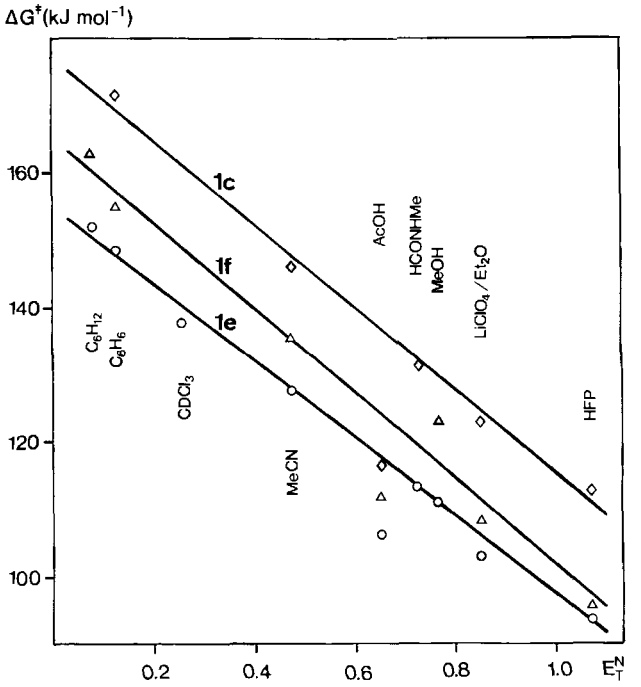


Figure 3. Correlation of free enthalpies of activation $\Delta G^{\neq}$ [kJ mol^{-1}] for the decomposition of the vinylcyclobutanes **1c**, **e** and **f** with Reichardt's polarity parameters E_T^N

exclude 100% stereospecific [2+2] cycloreversions but leave the possibility that rearrangements occur with a very high degree of stereospecificity.

In a given solvent, the fastest reactions have always been found for the rearrangements of the (*E*)-vinylcyclobutanes **1a** and **e**, which proceed at almost equal rates. The isomeric (*Z*)-vinylcyclobutanes **1b** and **f** rearrange more slowly, at a rate similar to that of the *cis*-vinylcyclobutane **1g**. The rates for the [2+2] cycloreversions of all diastereomeric vinylcyclobutanes **1e–h** are very similar. By far the smallest rate constants have been found for the rearrangements or [2+2] cycloreversions of the methacrylic cyclobutanes **1c**, **d**, **i** and **k**. The rates of a given vinylcyclobutane vary so strongly in different solvents that we have not been able to compare them at one temperature. We have chosen the free activation enthalpy $\Delta G^{\neq}$ for comparison and have selected temperatures which keep the rate constants between 10^{-3} and 10^{-5} s^{-1}. A good correlation (Figure 3) has been found for the $\Delta G^{\neq}$ values of the vinylcyclobutane **1e**, which has most carefully been investigated, and for Reichardt's solvent polarity constants[12,13] E_T^N, using the following equation.

$$\Delta G^{\neq} = [154.8 - 57.1\ E_T^N]\ [\text{kJ mol}^{-1}]$$

Only the values for acetic acid are markedly outside the correlation and have not been considered for the equation. Similar dependences have been found for the (*Z*) diastereomer **1f** with $\Delta G^{\neq}$ values which are 5–10 kJ mol^{-1} higher and for the methacrylic derivative **1c** with $\Delta G^{\neq}$ values which are approximately 20 kJ mol^{-1} higher than those of **1e**. These correlations have been established for the total reaction rate. The slope for the rearrangement alone is even a little steeper. The free activation enthalpies of the *trans*-vinylcyclobutanes **1e**, **f** and **1i**, **k** usually do not differ from those of their homologs **1a**, **b** and **1c**, **d**, respectively, by more than 5 kJ mol^{-1}. The *cis*-vinylcyclobutanes **1g** and **h**, on the other hand, decompose considerably slower than the *trans* diastereomers **1e** and **f**. By far the highest activation barriers have been found for the methacrylic cyclobutanes **1c**, **d**, **i** and **k**.

The rate differences between (*E*/*Z*) or *cis*/*trans*-vinylcyclobutanes are more pronounced for rearrangement than for [2+2] cycloreversion, indicating that steric demands are more important for rearrangement. The same conclusion may be drawn from the activation parameters (Table 9). While large negative values of approximately −100 J K^{-1}

Table 9. Activation parameters $\Delta H_R^{\neq}$ [kJ mol^{-1}] and $\Delta S_R^{\neq}$ [J mol^{-1} K^{-1}] for the rearrangement to the cyclohexenes **2** and $\Delta H_C^{\neq}$ [kJ mol^{-1}] and $\Delta S_C^{\neq}$ [J mol^{-1} K^{-1}] for the [2+2] cycloreversion to the dienoates **3** of the vinylcyclobutanes **1e**, **f** and **h**

1	Solvent	$\Delta H_R^{\neq}$	$\Delta S_R^{\neq}$	$\Delta H_C^{\neq}$	$\Delta S_C^{\neq}$
e	C_6D_6	106±3	−98±8	146±3	−17±5
	MeCN	88±2	−99±5		
	MeOH	74±6	−106±14		
f	C_6D_6	118±3	−86±9	140±3	−30±7
	a)	115±2	−97±6		
h	C_6D_6			130±4	−52±9

[a] Only the rearrangement to *trans*-cyclohexene **2d** is considered.

mol^{-1} have been found for the rearrangement of the (*E*)-vinylcyclobutane **1e** in such different solvents as benzene, acetonitrile or methanol, the [2+2] cycloreversion exhibits a much smaller value of only -17 J K^{-1} mol^{-1} in benzene. The two (*Z*)-vinylcyclobutanes **1f** and **h** behave similarly with large negative entropies of activation for rearrangement and smaller ones for [2+2] cycloreversion.

Acid catalysis gives rise to a tremendous increase of the reaction rates. Although we have not determined the reaction rates carefully, we may safely estimate that 30 mol-% of perchloric acid reduces the free enthalpy of activation for the ring opening of vinylcyclobutane **1c** in glacial acetic acid by more than 30 kJ mol^{-1}. Likewise, 12 mol-% of tin tetrachloride lowers the activation barrier for the rearrangement of vinylcyclobutane **1e** in acetonitrile by more than 50 kJ mol^{-1}.

Discussion

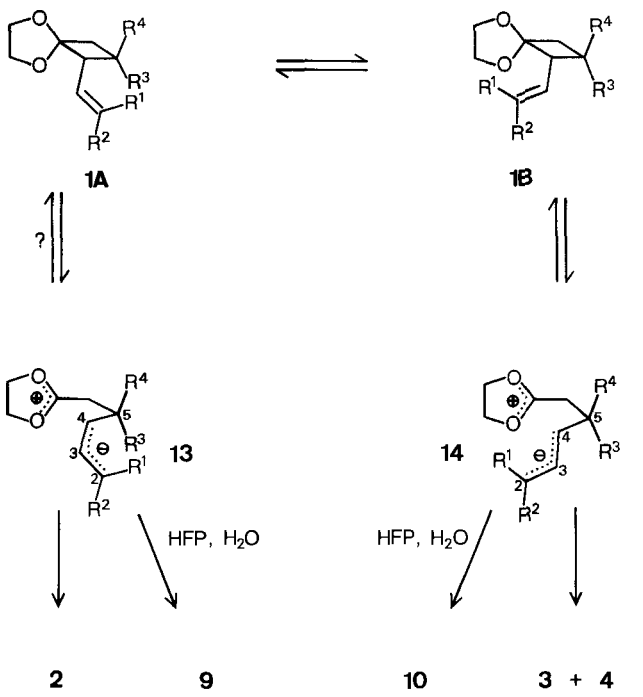
The missing stereospecificity leads to the conclusion that the vinylcyclobutane-cyclohexene rearrangement is not a concerted process but rather occurs via intermediates, which, owing to their substitution pattern, are best described as zwitterions **13**. The strong dependence of the reaction rate on solvent polarity corroborates the polar nature of these intermediates. Similar evidence for zwitterions with opposite charge distribution has already been found in other vinylcyclobutane-cyclohexene rearrangements[2]. The rates of [2+2] cycloreversions also increase with solvent polarity, suggesting the same intermediate for both reactions.

However, the different slopes of these correlations and the differences in stereospecificity and entropies of activation plead for two different types of zwitterions **13** and **14**, which do not interconvert rapidly.

Indeed, we have been able to prove that two different kinds of zwitterions occur in the reaction mixtures by trapping them with water in 1,1,1,3,3,3-hexafluoro-2-propanol to yield two different 3-heptenedioates **9c** and **10c**. The first and rate-determining step of this interception probably involves a protonation by 1,1,1,3,3,3-hexafluoro-2-propanol (pK_A: 9.37[9]), since water does not add to the zwitterions when aqueous methanol is used as solvent for the rearrangement of vinylcyclobutane **1e** and neither do the stronger nucleophiles methanol or thiophenol. The structures of these 3-heptenedioates prove unequivocally the (3*Z*) or (3*E*) geometries of the intermediates **13c** and **14c**. Only the (3*Z*) zwitterions **13** meet the requirements for ring closure to give cyclohexenes, while zwitterions **14** can only return to the vinylcyclobutanes **1** or break another bond to afford dioxolane **3** and dienoates **4**. With the 3-heptenedioate **10c** we have intercepted for the first time an intermediate of a vinylcyclobutane-cyclohexene rearrangement. Since the zwitterion trapped with a thiophenol by Nishida[2b] displays (*E*) geometry in the decisive bond of the allylic cation moiety it is *not* the precursor of a cyclohexene.

We propose that the (3*Z*) and (3*E*) zwitterions **13** and **14** are created by different routes, depending on the conformation **A** or **B** of the vinylcyclobutanes **1** with planar or

Scheme 1



The substituent key for the zwitterions **13** and **14** is the same as for the vinylcyclobutanes **1**

nearly planar arrangements of the bonds which later constitute the allylic part of the zwitterions when the ring is opened. The high steric demands of conformation **A** may be responsible for the large negative entropy of activation in the rearrangement, if the rate-determining step is the formation of the zwitterion **13**. The fact that the methacrylic derivatives **1c**, **d**, **i** and **k** prefer cycloreversion to rearrangement in most solvents can easily be explained within this picture. While the substantial increase in free activation enthalpy for rearrangement as well as for [2+2] cycloreversion of the methacrylic cyclobutanes compared to the acrylic homologs is mainly due to stabilizing or destabilizing effects of the additional methyl group in the vinylcyclobutanes **1** and both zwitterions **13** and **14**, the difference in the ratio of the two reactions may be traced to steric effects. Conformer **1A** with synperiplanar or at least synclinal arrangement of the double bond and one cyclobutane bond is strained, i.e. energetically unfavorable, if R^1 is a substituent other than hydrogen. This argument also holds true for the transition state of the ring opening. ^{1}H-NMR spectra show that the conformational equilibria[14] of the vinylcyclobutanes **1** change with substituents R^1 and R^3. The low populations of sterically constrained conformations **A** slow down the reaction rates of rearrangement, while the rates of [2+2] cycloreversion via conformers **1B** are not reduced but rather slightly enhanced. Higher reaction temperatures could raise the population of conformation **A**, but the competing [2+2] cycloreversion with small entropies of acti-

vation are even more accelerated. The same arguments may be applied to the (*Z*)-vinylcyclobutanes **1b** and **f**, and the *cis*-vinylcyclobutanes **1g** and **h**, where the ester (R^1) or methyl group (R^3) impairs conformation **A** and thus slows down rearrangement. In more polar solvents at lower temperatures, which are not sufficient to induce [2+2] cycloreversion, ring enlargement is possible at a comparable slow rate.

The four diastereomeric vinylcyclobutanes **1e–h** are transformed into eight different zwitterions, which can in principle conserve the stereochemical information of the precursors. Indeed, the [2+2] cycloreversions via **14e–h** occur with more than 75% stereospecificity, and the ring enlargement also shows stereospecificities of more than 60% for **1e–g** in benzene. In more polar solvents, the relatively long lifetimes of the zwitterions allow for rotations to compete more effectively with rearrangement. Thus, stereospecificity is reduced and may be lost totally.

Diastereomerization of the vinylcyclobutanes is slower than rearrangement for **1e**, about equal for **1c**, **f**, **g** and **i**, and faster for **1d** and **k**. In principle, rotations in both zwitterions **13** and **14** may be responsible for the diastereomerization of the vinylcyclobutanes and the loss in stereospecificity in rearrangement and [2+2] cycloreversion, but it is more likely that mainly the (3*E*) diastereomers **14** are involved. The Hammond principle[15] leads to the conclusion that the ring closure of (3*Z*) zwitterions **13** to reform vinylcyclobutanes **1** should require considerably higher energies of activation than the alternative route to give cyclohexenes **2** with approximately 100 kJ mol^{-1} less strain energy in the parent compound[16]. This means that most zwitterions **13** do not return to vinylcyclobutanes **1** and cannot be responsible for diastereomerization observed unequivocally for **1c/d** and **1i/k** in $LiClO_4$/diethyl ether. Besides, the lifetimes of the (*Z*) zwitterions **13** are probably too short to allow for rotations. It thus seems reasonable to assume that diastereomerization and thereby loss in stereospecifity occur primarily in the (3*E*) zwitterions **14**.

Both the above reasoning and experimental evidence support this hypothesis. It is possible to construct kinetic systems which simulate all experimental results by assuming 100% stereospecific vinylcyclobutane-cyclohexene rearrangements. 100% stereospecific [2+2] cycloreversions, however, are not in agreement with experiments, regardless of the kinetic system. The product-determining, and probably also the rate-determining, step for the [2+2] cycloreversion is the breaking of the second cyclobutane bond and not the formation of the zwitterion **14**. This is necessarily true for the vinylcyclobutanes **1i** and **k**, where rotations in the zwitterions **14i** or **k** must occur at least twenty times or one hundred times more often than bond breaking to account for the stereochemical results. The small values for the entropies of activation are also in accordance with this mechanism.

The stereochemical results of the rearrangement of (*trans,E*)-vinylcyclobutane **1e** suggest that the migration occurs in a least-motion mode, suprafacially and without any noticeable rotations in the allylic parts of the zwitterions **13e** and **14e**. The symmetry of the dioxolane ring does not allow its rotation (≡ inversion of the migrating carbon) being ruled out, but in a closely related system with a stereochemical label no inversion is observed[17]. This means violation of the Woodward-Hoffmann[18] rules for a concerted 1,3-sigmatropic shift. On the other hand, rotation around the allylic bonds 2 of (3*E*) zwitterions **14f** to give **14e** and **14k** to give **14i** is faster than ring enlargement via (3*Z*) zwitterions **13f** or **13i**, respectively, in polar media, indicating that the (2*E*) configuration is more stable than the (2*Z*) configuration in both zwitterions, which seems reasonable[19]. Rotation around bond 4 in the zwitterions **14** derived from *trans*-vinylcyclobutanes **1e** and **f** is only observed in the cycloreversion products **4** with less than 8%. In the zwitterions **14** derived from the *cis*-vinylcyclobutane **1g**, on the other hand, we must assume rotation around bond 4 to explain the formation of *trans*-vinylcyclobutane **1e** and of *cis*-cyclohexene **2c**. The yield of **2c** increases with solvent polarity from 3% in benzene to 64% in acetonitrile and 71% in methanol. This suggests that the energetically unfavorable *cis* relationship in the vinylcyclobutanes **1g** and **h** still exists in the zwitterions **14g** and **h**. Although we don't want to stress this point too much, the steric constraints in the zwitterions **14f** and **h** may also be responsible for the higher activation entropies for cycloreversion of **1f** and **h** in comparison with **1e**.

Scheme 2

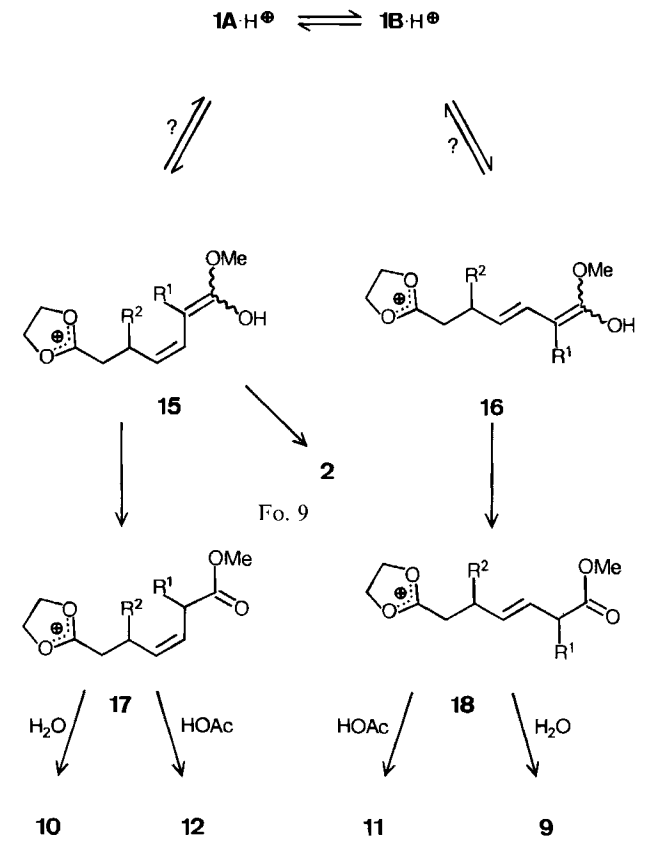


Fig. 9

The substituent key for the dioxolanium ions **15**, **16**, **17** and **18** is the same as for the heptadienoates **9**, **10**, **11** and **12**

These results show that there is a considerable barrier to rotation around bonds 2 and 4 in the zwitterions **14**, the former being attributed to stabilization in an ester enolate system, the latter to interaction of the charge centers. Polar media stabilize the zwitterions through solvation of the charge centers, thus facilitating rotations in two ways: the lifetime of the zwitterions is extended, and the importance of internal charge compensation is reduced.

While good correlation between free enthalpies of activation and solvent parameters E_T^N have been found for most solvents, acetic acid shows strong deviations from these correlations. Moreover, in acetic acid side products **9** and **11** are formed, seemingly by addition of water or acetic acid to the zwitterions. The reason for the faster than expected rearrangement and the side products in acetic acid may be due to a change in mechanism. With stronger acids like perchloric acid and Lewis acids the rate acceleration is more pronounced. The activation energy is lowered by as much as 50 kJ mol^{-1}. A strong influence of acid catalysis is predicted for ring opening of related cyclobutanes[20]. The first step of the acid catalysis involves protonation of the carbonyl oxygen followed by ring opening to dioxolanium ions[21] **15** and **16**, which carry on the end of the 2-substituent a nucleophilic vinylketene O,O-acetal moiety, capable of attacking the cationic center. As the intramolecular attraction and high rotation barriers of the zwitterions **13** and **14** are lost in the cationic intermediates **15** and **16**, no stereospecificity or stereoselectivity can be expected, and, indeed, roughly random mixtures (between 60:40 and 50:50) of cyclohexenes **2c/d** and **e/f** or addition products **9e/f** and **11e/f** are formed. Like the zwitterions **14**, the (*E*) intermediates **16** have the wrong configuration for cyclohexene formation and can only return to four-membered rings or add nucleophiles like acetic acid and water. The first step of the addition reactions must be a protonation of the vinylketene acetal moiety to give protonated esters **17** and **18**. Stronger nucleophiles like thiophenol do not increase the yield of addition products, in contrast to stronger acids. There is also spectrometric evidence for the formation of such intermediates. The mixtures of vinylcyclobutane **1c** in 0.1 N $HClO_4$ in glacial acetic acid gives rise to transient signals in the ^{1}H-NMR spectra, which account for 35% of the starting material after 15 minutes. We assign a singlet at $\delta = 5.56$ to the dioxolanium protons of intermediate **18b**. The vinylketene acetal is only protonated on the β carbon and never on the δ carbon, not even in a reversible reaction. After the thermolysis of **1a** in perdeuterated acetic acid, no incorporation of deuterium has been found on C-4 of the heptenedioate **11a** or in the cyclohexene **2a**. In pure acetic acid, the dioxolanium acetates **15a** and **c** with the appropriate (*Z*) configuration in the allylic part apparently close the cyclohexene ring too fast to be intercepted by acetic acid. In perchloric acid catalyzed reactions, however, the (*Z*)-configurated dioxolanium perchlorates **15a** and **c** are also trapped by acetic acid to afford (*Z*)-heptenedioates **12a** and **c**, respectively. Likewise, in the tin tetrachloride catalyzed rearrangement of vinylcyclobutane **1e**, a (*Z*) intermediate is trapped by water to afford the heptenedioate **10c**. In the reaction of **1a** with 0.1 N $HClO_4$ in glacial acetic acid, the heptenedioates **9a** and **10a** are formed at the same time as cyclohexene **2a**, i.e. under actual rearrangement conditions, hence corroborating the idea that **15a** indeed is an intermediate of the rearrangement.

Why can 1,1,1,3,3,3-hexafluoro-2-propanol (HFP, $pK_A = 9.3$) intercept a (*Z*) intermediate and acetic acid ($pK_A = 4.75$) cannot? This result also corroborates our assignment of different mechanisms. In HFP we may well have a mixed mechanism. The reaction rate, which correlates well with Reichardt's E_T^N value, suggests that the reaction starts with the formation of zwitterions **13c** and **14c**. HFP is *not* acidic enough to protonate vinylcyclobutane **1e** and catalyze bond breakage. However, the acidity of HFP is sufficient to protonate the *ester enolate* moieties of zwitterions **13e** and **14e** either on oxygen or on C-2. While *C*-protonation and addition of water leads to heptenedioates **9c** and **10c**, *O*-protonation to give **15c** and **16c** ends in the acid-catalyzed reaction. Acetic acid on the other hand catalyzes the ring opening. This means that dioxolanium acetates **15c** and **16c** occur as intermediates. The acidity of acetic acid does not suffice to protonate the *ester enol* moiety of (*Z*)-dioxolanium acetate **15c** fast enough to compete with ring closure.

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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) and 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^2) with 1-mm layers of silica gel $PF_{254,366}$ (Merck) were used. — Simulations and iterative optimizations of ^{1}H-NMR spectra were performed by means of the computer program DAVINS[22].

Dry Solvents: Benzene, cyclohexane, diethyl ether and THF were freshly distilled from sodium hydride. *N*-methylformamide and acetonitrile were distilled from calcium hydride. Methanol was purified with magnesium. Deuterated solvents were kept under argon and dried over molecular sieves. Glacial acetic acid and 0.1 N $HClO_4$ in glacial acetic acid were used as purchased.

For thermolyses in $LiClO_4$/diethyl ether stock solutions were prepared and aliquots used: $LiClO_4$ was desiccated over P_4O_{10} at 140°C for 15 h. 6.65 g (62.5 mmol) of this $LiClO_4$ was dissolved in 12.5 ml of dry diethyl ether to give a clear solution within a few seconds. Cloudy solutions were discarded.

Vinylcyclobutanes **1**[14], dioxolane **3**[8], hexadienoates **4e**[23a], **f**[23b], **g**[23c], **h**[23d], **i**[24] and **k**[24], and acetates **6**[8] and **7**[25] were prepared according to literature procedures.

2-[2-Methyl-1,3-dioxolan-2-yloxy]ethyl Acetate (**8**): 135 mg (7.49 mmol) of water was added to 1.72 g (20.0 mmol) of dioxolane **3** in 20 ml of 2-methyl-2-propanol. After heating the mixture at reflux for 2 h, fractionating distillation at 18 Torr yielded 1.04 g (73%) of acetate **8** with b.p. 105–106°C. — IR (film): $\tilde{\nu} = 1740\ cm^{-1}$. —

^{1}H NMR (80 MHz, CCl_4): δ = 1.43 (s, dioxolane Me), 1.98 (s, acetate Me), 3.4–4.3 (m, 4 OCH_2). – MS: *m/z* = 190 (M^+).

$C_8H_{14}O_5$ (190.2) Calcd. C 50.52 H 7.42
Found C 50.58 H 7.40

a) A solution of the ortho ester **8** in $CDCl_3$ was covered with a layer of water. After 16 h, only a mixture of esters **6** and **7** (11:89) was identified (^{1}H NMR).

b) A solution of 90 mg (424 μmol) of vinylcyclobutanes **1c** and **d** (87:13) in 0.5 ml of moist acetonitrile was heated to 165°C for 12 h in a sealed tube. The solvent was removed in vacuo and the remaining colorless oil distilled at 10^{-3} Torr/80–120°C bath temperature to give 79 mg of a 52:48 mixture of cyclohexene **2c** [87%, ⩾ 95% (*E*)] and ortho ester **8** (81%).

Methyl 1,4-Dioxaspiro[4.5]dec-7-ene-6-carboxylate (**2a**): A solution of 323 mg (1.63 mmol) of vinylcyclobutane **1a** in 1.5 ml of acetonitrile was heated to 124°C for 2 h in a sealed tube. The solution was concentrated in vacuo and the remaining oil purified by chromatography on silica gel with diethyl ether/pentane (25:75) to yield 310 mg (96%, R_f = 0.25) of cyclohexene **2a** as a colorless oil.

Methyl 6-Methyl-1,4-dioxaspiro[4.5]dec-7-ene-6-carboxylate (**2b**): A clear solution of 185 mg (872 μmol) of vinylcyclobutanes **1c** and **d** (44:56) and 798 mg of $LiClO_4$ in 1.50 ml of dry diethyl ether was heated to 87°C in a sealed tube for 69 h. The mixture was poured on 3 ml of water and extracted with 3 × 5 ml of diethyl ether. The organic phase was dried over anhydrous K_2CO_3 and concentrated in vacuo to give a colorless oil. Purification on silica gel with diethyl ether/pentane (35:65) afforded 146 mg (79%, R_f = 0.3) of cyclohexene **2b**. – IR (film): $\tilde{\nu}$ = 1737 cm^{-1} (C=O), 1653 (C=C). – MS (70 eV): *m/z* (%) = 212 (17) [M^+], 86 (100).

Methyl cis-9-Methyl-1,4-dioxaspiro[4.5]dec-7-ene-6-carboxylate (**2c**): A solution of 121 mg (570 μmol) of vinylcyclobutane **1e** in 1 ml of methanol was heated to 100°C for 3 h in a sealed tube. The solution was concentrated in vacuo and the remaining oil distilled at 10^{-3} Torr/85–95°C bath temperature to yield 113 mg (96%) of cyclohexene **2c** as a colorless oil. – IR (film): $\tilde{\nu}$ = 1737 cm^{-1} (C=O), 1654 (C=C). – MS (20 eV): *m/z* (%) = 212 (25) [M^+], 86 (100).

Methyl trans-9-Methyl-1,4-dioxaspiro[4.5]dec-7-ene-6-carboxylate (**2d**):

a) A solution of 109 mg (514 μmol) of the vinylcyclobutane **1f** in 0.8 ml of methanol was heated to 106°C for 5 h in a sealed tube. The solution was concentrated in vacuo and the remaining oil separated by chromatography on silica gel with diethyl ether/pentane (30:70) to yield 69 mg (63%, R_f = 0.25) of *cis*-cyclohexene **2c** and 31 mg (28%, R_f = 0.20) of *trans*-cyclohexene **2d** as colorless oils.

b) To a solution of 50.4 mg (193 μmol) of $SnCl_4$ in 1.5 ml of acetonitrile 330 mg (1.56 mmol) of the vinylcyclobutane **1e** was added at 0°C under argon. After 3.5 h at room temperature, the mixture was poured onto 5 ml of water and extracted with 3 × 5 ml of diethyl ether. The organic phases were dried over K_2CO_3 and concentrated in vacuo. Chromatography on silica gel with diethyl ether/pentanes (40:60) afforded 141 mg (43%, R_f = 0.35) of the *cis*-cyclohexene **2c**, 146 mg (44%, R_f = 0.30) of the *trans*-cyclohexene **2d** and 36 mg (10%, R_f = 0.10) of the heptenedioates **9c** and **10c** (55:45). – IR (film): $\tilde{\nu}$ = 1736 cm^{-1} (C=O), 1654 (C=C).

Methyl cis/trans-6,9-Dimethyl-1,4-dioxaspiro[4.5]dec-7-ene-6-carboxylates (**2e, f**):

a) A clear solution of 269 mg (1.19 mmol) of vinylcyclobutane **1i** and 1.06 g of $LiClO_4$ in 1.5 ml of diethyl ether was heated to 96°C for 5 d in a sealed tube. 3 ml of water was added, and the mixture was extracted with 3 × 5 ml diethyl ether. After drying over anhydrous K_2CO_3 and concentration in vacuo the remaining oil was chromatographed on silica gel with diethyl ether/pentanes (35:65) as eluent to afford 199 mg (74%, R_f = 0.4) of a mixture of cyclohexenes **2e** and **f** (93:7).

b) A solution of 128 mg (566 μmol) of vinylcyclobutanes **1i** and **k** (65:35) and 14.7 mg (56.6 μmol) $SnCl_4$ in 0.4 ml of acetonitrile was heated to 93°C in a sealed tube for 17 h. 2 ml of water was added and the mixture extracted with 3 × 5 ml of diethyl ether. After drying over anhydrous K_2CO_3, the solvent was evaporated. Separation on silica gel with diethyl ether/pentanes (25:75) as eluent afforded 33 mg (26%, R_f = 0.30) of the *cis*-cyclohexene **2e**, 67 mg (52%, R_f = 0.25) of the *trans*-cyclohexene **2f** and 19 mg (14%, R_f = 0.1) of the heptenedioates **9d** and **e**. – IR (**2e**, film): $\tilde{\nu}$ = 1732 cm^{-1} (C=O), 1657 (C=C). – MS (70 eV): *m/z* (%) = 226 (12) [M^+], 86 (100).

O^7-(2-Hydroxyethyl) O^1-Methyl (3E)-Heptenedioate (**9a**): A solution of 70.0 mg (353 μmol) of the vinylcyclobutane **1a** in 0.5 ml of moist acetic acid was heated to 80°C for 2 h. After evaporation of the solvent, the remaining oil was dissolved in 10 ml of diethyl ether, dried over anhydrous K_2CO_3, concentrated in vacuo and chromatographed on silica gel with diethyl ether/pentanes (35:65) as eluent to give 40 mg (57%, R_f = 0.35) of the cyclohexene **2a** and 27 mg (35%, R_f = 0.1) of the heptenedioate **9a** as colorless oils. A solution of 27 mg (125 μmol) of the heptenedioate **9a** and 39 mg (497 μmol) of acetyl chloride in 0.5 ml of $CDCl_3$ was kept at room temperature for 20 h. The ^{1}H-NMR spectrum showed only signals of the heptenedioate **11a**.

O^7-(2-Hydroxyethyl) O^1-Methyl (3E)-2-Methyl-3-heptenedioate (**9b**): A solution of 104 mg (490 μmol) of vinylcyclobutane **1c** in 0.5 ml of moist acetic acid was heated to 80°C for 30 h. After evaporation of the solvent, the remaining oil was dissolved in 10 ml of diethyl ether, dried over anhydrous K_2CO_3, concentrated in vacuo and chromatographed on silica gel with diethyl ether/pentanes (65:35) as eluent to give 68 mg (60%, R_f = 0.15) of the heptenedioate **9b** and 44 mg (33%, R_f = 0.45) of the heptenedioate **11b**. A solution of 44 mg (162 μmol) of the heptenedioate **9b** and 79 mg (1.01 mmol) of acetyl chloride in 0.5 ml of $CDCl_3$ was kept at room temperature for 18 h. The ^{1}H-NMR spectrum showed only signals of the heptenedioate **11b**.

O^7-(2-Hydroxyethyl) O^1-Methyl (3E)-5-Methyl-3-heptenedioate (**9c**): A solution of 45.0 mg (227 μmol) of vinylcyclobutane **1f** in 0.5 ml of moist acetic acid was heated to 80°C for 2 h. After evaporation of the solvent, the remaining oil was dissolved in 10 ml of diethyl ether, dried over anhydrous K_2CO_3, concentrated in vacuo and chromatographed on silica gel with diethyl ether/pentanes (35:65) as eluent to give 8 mg (18%, R_f = 0.35) of the cyclohexenes **2c** and **d** (55:45) and 36 mg (73%, R_f = 0.1) of the heptenedioate **9c**. A solution of 36 mg (167 μmol) of the heptenedioate **9c** and 39 mg (497 μmol) of acetyl chloride in 0.5 ml of $CDCl_3$ was kept at room temperature for 20 h. The ^{1}H-NMR spectrum showed only signals of the heptenedioate **11c**.

O^7-(2-Hydroxyethyl) O^1-Methyl (3E,Z)-5-Methyl-3-heptenedioates (**9c, 10c**):

a) A solution of 34 mg (160 μmol) of the vinylcyclobutane **1e** in 0.5 ml of 1,1,1,3,3,3-hexafluoro-2-propanol was kept at 22°C for 18 h. The solvent was evaporated and the remaining oil separated on silica gel with diethyl ether/hexanes (40:60) as eluent to yield 15 mg (44%, R_f = 0.30) of the cyclohexene **2c**, 7 mg (21%, R_f = 0.25) of the cyclohexene **2d** and 11 mg (30%, R_f = 0.05) of a 42:58

mixture of the (*E,Z*)-heptenedioates **9c** and **10c**. 20 mg (255 μmol) of acetyl chloride was added to the solution of 11 mg (48 μmol) of **9c** and **10c** in 0.5 ml of $CDCl_3$. After standing for 24 h, the ratio of the only products was determined from the ^{1}H-NMR spectrum as **11c**:**12c** = 42:58.

b) A solution of 30 mg (140 μmol) of the vinylcyclobutane **1e** and 26 mg (10 μmol) of $SnCl_4$ in 0.5 ml of moist acetonitrile was kept at 0°C for 7 h. After addition of 5 ml of diethyl ether, the solution was extracted with dilute NaOH and water, dried over K_2CO_3 and concentrated in vacuo. The remaining oil contained 24 mg (73%) of the heptenedioates **9c** and **10c** (55:45, ^{1}H NMR).

O⁷-(2-Hydroxyethyl) O¹-Methyl (3E)-2,5-Dimethyl-3-heptenedioates (**9d, e**): To a solution of 104 mg (339 μmol) of $SnCl_4$ in 2 ml of acetonitrile 176 mg (778 μmol) of vinylcyclobutane **1i** was added under nitrogen at 0°C. After 1 h at 20°C, the mixture was poured on water and extracted with 3 × 5 ml of diethyl ether. The combined organic phases were washed with aqueous $NaHCO_3$ and water, dried over anhydrous K_2CO_3, concentrated in vacuo and chromatographed on silica gel with diethyl ether/pentanes (40:60) as eluent to give 152 mg (80%, R_f = 0.1) of the heptenedioates **9d** and **e** (60:40). 157 mg (2.00 mmol) of acetyl chloride was added to a solution of 152 mg (622 μmol) of **9d** and **e** in 2 ml of $CDCl_3$. After standing for 24 h, the ratio of the products was determined from the ^{13}C-NMR spectrum as **11d**:**e** = 60:40.

Table 10. Analytical data of the cyclohexenes **2** and the 3-heptenedioates **11** and **12**

	Formula	Mol. mass	C Calcd.	C Found	H Calcd.	H Found
2a	$C_{10}H_{14}O_4$	(198.2)	60.59	60.65	7.12	7.36
b	$C_{11}H_{16}O_4$	(212.2)	62.25	62.48	7.60	7.57
c	$C_{11}H_{16}O_4$	(212.2)	62.25	62.53	7.60	7.42
d	$C_{11}H_{16}O_4$	(212.2)	62.25	62.25	7.60	7.32
e,f	$C_{12}H_{18}O_4$	(226.3)	63.70	63.81	8.02	7.99
11,12a	$C_{12}H_{18}O_6$	(258.3)	55.81	56.08	7.03	7.07
11b	$C_{13}H_{20}O_6$	(272.3)	57.34	57.60	7.40	7.16
11,12c	$C_{13}H_{20}O_6$	(272.3)	57.34	57.56	7.40	7.06
11d,e	$C_{14}H_{22}O_6$	(286.3)	58.73	58.59	7.74	8.11

O⁷-(2-Acetoxyethyl) O¹-Methyl (3E)-Heptenedioate (**11a**): A solution of 75.0 mg (379 μmol) of the vinylcyclobutanes **1a** and **b** (62:38) in 0.5 ml of glacial acetic acid and 0.02 ml of acetic anhydride was heated to 80°C for 3.5 h. After evaporation of the solvent, the remaining oil was dissolved in 10 ml of diethyl ether, dried over anhydrous K_2CO_3, concentrated in vacuo and chromatographed on silica gel with diethyl ether/pentanes (30:70) as eluent to give 45 mg (60%, R_f = 0.25) of the cyclohexene **2a** and 34 mg (35%, R_f = 0.20) of the heptenedioate **11a**.

O⁷-(2-Acetoxyethyl) O¹-Methyl (3E,Z)-Heptenedioates (**11a, 12a**): 416 mg (2.10 mmol) of the vinylcyclobutane **1a** was dissolved in 2.0 ml of 0.1 N $HClO_4$/HOAc under nitrogen at 0°C and kept at room temperature for 1 h. The solution was poured on 5 ml of water and the mixture extracted with 3 × 5 ml of diethyl ether. The combined organic phases were washed with aqueous $NaHCO_3$ and water, dried over anhydrous K_2CO_3, concentrated in vacuo and chromatographed on silica gel with diethyl ether/pentanes (25:75) as eluent to give 223 mg (41%, R_f = 0.22) of the heptenedioates **11a** and **12a** (34:66) and 211 mg (44%, R_f = 0.25) of a mixture of **2a**, **11a** and **12a** (48:18:34). – IR (**11a, 12a**, film): $\tilde{\nu}$ = 1739 cm^{-1} (C=O).

O⁷-(2-Acetoxyethyl) O¹-Methyl (3E)-2-Methyl-3-heptenedioate (**11b**):

a) A solution of 80.0 mg (0.377 mmol) of vinylcyclobutane **1c** in 0.5 ml of glacial acetic acid and 0.02 ml of acetic anhydride was heated to 80°C for 30 h. After evaporation of the solvent, the remaining oil was dissolved in 10 ml of diethyl ether, dried over anhydrous K_2CO_3, concentrated in vacuo and chromatographed on silica gel with diethyl ether/pentanes (35:65) as eluent to give 90.3 mg (88%, R_f = 0.35) of the heptenedioate **11b**.

b) 36 mg (170 μmol) of the vinylcyclobutane **1c** was dissolved at 0°C under argon in 0.5 ml of 0.1 N $HClO_4$/HOAc. After 15 min at room temperature, the ^{1}H-NMR analysis showed 28% of the vinylcyclobutane **1c**, 37% of the heptenedioate **11b** and 35% of the dioxolanium perchlorate **18b** (s, δ = 5.56). Within another 45 min this mixture had changed to 85% of **11b** and 15% of **18b**. After 5 h, the solution was diluted with 10 ml of diethyl ether, extracted with 10 ml of 2 N NaOH and water, dried over K_2CO_3 and concentrated in vacuo to give 44 mg (95%) of a colorless oil which, according to the ^{1}H-NMR spectrum, was virtually pure **11b**. – IR

Table 11. Chemical shifts δ_H of the cyclohexenes **2** in CCl_4 determined from 80-MHz ^{1}H-NMR spectra

2	2,3-H	6-R	7-H	8-H	9-H	9-R	10-H_A	10-H_B	OMe
a	3.89	3.11	5.43	5.77	2.1 - 2.4		2.1	1.56	3.59
b	3.89	1.21	5.49	5.70	2.1 - 2.3		1.88	1.65	3.60
c	3.88	3.01	5.34	5.59	2.41	1.03	1.89	1.58	3.59
a)	4.05	3.23	5.56	5.79	2.53	1.10	2.01	1.76	3.75
d	3.88	3.20	5.44	5.58	2.49	0.99	2.02	1.32	3.60
a)	4.05	3.50	5.65	5.79	2.61	1.06	2.09	1.46	3.76
e	3.88	1.25	5.17	5.45	2.33	1.03	1.93	1.62	3.58
f	3.88	1.40	5.36	5.51	2.40	0.99	1.73	1.35	3.59

[a] In $CDCl_3$ (100 MHz).

Table 12. Coupling constants J_{HH} [Hz] of the cyclohexenes **2** in CCl_4 determined from 80-MHz ^{1}H-NMR spectra

2	6,7	6,8	6,9	6,10B	7,8	7,9	8,9	8,10B	9,10A	9,10B	9,R	10A,10B
a	4.0	2.0	3.6[a]		10.2	3.2[a]	6.0[a]					
b					10.6[a]	6.0						
c	4.4	1.3	2.6	1.4	9.9	2.6	1.8	0.9	10.8	5.7	7.2	13.0
b)	4.57	1.38	2.42	1.64	9.85	-2.64	2.12	0.97	10.93	5.69	7.20	-12.92
d	2.6	1.9	3.6	0.8	10.0	1.6	2.3		5.7	7.3	7.1	13.1
c)	2.91	-2.44	3.02	0.78	9.99	-2.47	2.58	0.24	5.83	8.90	7.23	-13.26
e					9.9	2.4	1.9	0.9	11.0	5.9	6.9	13.0
f[d]					10.5	1.5	2.5		5.5	9.9	7.0	13.2

[a] $J_{9A} + J_{9B}$. — [b] In $CDCl_3$ (100 MHz). — [c] In $CDCl_3$ (100 MHz), $J_{8,10A} = 0.77$ Hz. — [d] $J_{8,10A} = 1.0$ Hz.

Table 13. Chemical shifts δ_C of the cyclohexenes **2** in $CDCl_3$ determined from $^{13}C\{^1H\}$-NMR spectra (20.15 MHz). All signals show the expected multiplicities in the off-resonance spectra

2	C-2, C-3	C-5	C-6	C-7	C-8	C-9	C-10	C=O	OMe	6-Me	9-Me
a	64.6, 65.0	107.6	50.7	122.4	129.6	24.3	29.0	171.3	52.0		
b	65.1, 65.3	109.9	52.0	130.1	129.7	24.2	28.4	174.0	52.2	20.7	
c	64.4, 64.8	108.0	50.6	120.9	136.3	30.4	36.9	171.3	52.1		20.7
d	64.7, 65.2	108.4	50.1	121.5	134.6	30.0	39.6	171.3	52.1		20.7
e	65.2, 65.2	109.9	52.2	128.6	133.8	30.3	37.3	173.7	52.2	18.2	20.7
f	64.8, 64.8	110.7	51.4	129.2	131.3	29.9	37.1	173.9	52.2	23.5	20.9

Table 14. Chemical shifts δ_H (s or m_c) and in parantheses coupling constants J [Hz] in CCl_4 of the 3-heptenedioates **9**, **10**, **11** and **12** determined from 80-MHz ^{1}H-NMR spectra

	2-H	3,4-H	5,6-H	O-Me	$O-CH_2$		Nu	2-Me	5-Me
9a	3.05	5.67	2.42	3.66	3.78	4.18	2.30		
b	2.98	5.51	2.38	3.62	3.77	4.19	2.21	1.18 (7.1)	
c	2.94	5.42	2.27	3.60	3.64	4.08	1.97		1.04 (7.1)
d,e	2.99	5.38	2.2 - 2.7	3.60	3.67	4.07	2.25	1.22 (7.6)	1.07 (6.5)
10c	3.05	5.42	2.27	3.60	3.64	4.08	1.97		1.08 (6.9)
11a	2.93	5.53	2.35	3.63	4.17		2.00		
b	3.00	5.57	2.41	3.67	4.30		2.03	1.21 (7.0)	
c	2.91	5.40	2.26	3.61	4.14		2.00		1.06 (6.4)
d,e	2.97	5.42	2.2 - 2.6	3.57	4.11		1.99	1.19 (7.7)	1.05 (6.4)
12a	3.03	5.53	2.35	3.63	4.17		2.00		
c	3.05	5.40	2.24	3.61	4.14		2.00		1.08 (6.4)

(film): $\tilde{\nu}$ = 1738 cm^{-1} (C=O). — MS (70 eV): *m/z* (%) = 272 (2) [M^+], 87 (100).

O^7-(2-Acetoxyethyl) O^1-Methyl (3E)-5-Methyl-3-heptenedioate (**11c**): A solution of 45.0 mg (212 µmol) of the vinylcyclobutane **1f** in 0.5 ml of glacial acetic acid and 0.02 ml of acetic anhydride was heated to 80°C for 3 h. After evaporation of the solvent, the remaining oil was dissolved in 10 ml of diethyl ether, dried over anhydrous K_2CO_3, concentrated in vacuo and chromatographed on silica gel with diethyl ether/pentanes (20:80) as eluent to give 7 mg (16%, R_f = 0.25) of the cyclohexene **2c** and 42 mg (73%, R_f = 0.20) of the heptenedioate **11c**. — IR (film): = 1740 cm^{-1} (C=O). — MS (70 eV): *m/z* (%) = 272 (19) [M^+], 87 (100).

O^7-(2-Acetoxyethyl) O^1-Methyl (3E,Z)-5-Methyl-3-heptenedioates (**11c, 12c**): 312 mg (1.47 mmol) of the vinylcyclobutane **1e** was dissolved in 1.5 ml of 01. N $HClO_4$/HOAc under nitrogen at 0°C and kept at room temperature for 1 h. The solution was poured on 5 ml of water and the mixture extracted with 3 × 10 ml of diethyl ether. The combined organic phases were washed with aque-

Table 15. Chemical shifts δ_C of the 3-heptenedioates **9**, **11** and **12** in $CDCl_3$ determined from $^{13}C\{^1H\}$-NMR spectra (20.15 MHz). All signals showed the expected multiplicities in the off-resonance spectra

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	OMe	O-CH_2	OAc	2-Me	5-Me
9d	175.4	42.6	128.2	135.5	33.7	41.6	172.6	51.9	61.1 65.9		17.5	20.2
9e	175.3	42.5	128.3	135.6	33.6	41.5	172.6	51.9	61.1 65.9		17.4	20.2
11a	172.0	37.7	123.1	132.2	27.7	33.6	172.6	51.8	62.2 62.2	170.7, 20.7		
11b	175.1	a)	129.7	130.2	27.6	33.7	172.6	51.7	62.1 62.1	170.7, a)	17.3	
11c	172.0	37.7	121.1	138.0	33.4	41.3	172.0	51.8	62.0 62.0	170.6, 20.7		19.9
11d,e[b]	175.1	42.6	128.2	135.5	33.4	41.4	172.0	51.7	62.0 62.2	170.6, 20.7	17.4	19.9
12a	172.0	32.7	122.5	130.9	22.8	33.6	172.6	51.9	62.2 62.2	170.7, 20.7		
12c	172.1	32.8	120.8	136.9	29.2	41.5	172.1	51.8	62.2 62.2	170.6, 20.7		20.5

[a] Signal not found, reaction with CD_3CO_2D. — [b] Both diastereomers had the same set of signals at 20.15 MHz. At 50.3 MHz two signals were found for C-5 (33.12, 33.17), C-2 (42.29, 42.33) and C-3 (128.04, 128.08).

Table 16. Free enthalpy of activation $\Delta G^{\neq}$ [kJ mol^{-1}] and in parentheses temperature [K] for the decomposition of the vinylcyclobutanes **1**. The last digit given is uncertain.

1	**a**	**b**	**c**	**e**[a]	**f**	**i**
cC_6H_{12}				152 (173)	164 (202)	
C_6D_6	149.1 (453)	153.3 (453)	172 (488)	148.5 (433)	152.7 (446)	
MeCN	123.6 (397)		147 (438)	127.6 (400)	135.4 (417)	
HCONHMe			132 (435)	113 (388)		137 (418)
MeOH	109.2 (353)			110.9 (373)	122 (373)	128.5 (415)
AcOH	106.3 (353)	110.5 (353)	116.7 (353)	106.3 (353)	111.7 (353)	124.3 (393)
$LiClO_4$/ Et_2O			123 (357)	103 (343)	108 (343)	126.5 (369)
HFP			115 (343)	94 (295)	96 (295)	

[a] $CDCl_3$: 137.7 (396).

ous $NaHCO_3$ and water, dried over anhydrous K_2CO_3, concentrated in vacuo and chromatographed on silica gel with diethyl ether/pentanes (20:80) as eluent to give 352 mg (88%, R_f = 0.2) of the heptenedioates **11c** and **12c** (37:63).

O'-(2-Acetoxyethyl) O'-Methyl (3E)-2,5-Dimethyl-3-heptenedioates (**11d, e**): 152 mg (0.672 mmol) of the vinylcyclobutane **1i** was dissolved in 0.7 ml of 0.1 N $HClO_4$/HOAc under nitrogen at 0°C and kept at room temperature for 1.5 h. The solution was poured on 5 ml of water and the mixture extracted with 3 × 5 ml of diethyl ether. The combined organic phases were washed with aqueous $NaHCO_3$ and water, dried over anhydrous K_2CO_3, concentrated in vacuo and chromatographed on silica gel with diethyl ether/pentanes (40:60) as eluent to give 169 mg (88%, R_f = 0.4) of the heptenedioates **11d** and **e** (50:50). — IR (film): $\tilde{\nu}$ = 1738 cm^{-1} (C=O). — MS (70 eV): *m/z* (%) = 286 (2) [M^+], 87 (100).

Kinetics: Solutions of 0.3–1.1 mmol of vinylcyclobutanes **1** and 0.1–0.3 mmol of internal standard (TMS or dimethyl phthalate) in 0.5–1.0 ml of solvent were sealed in NMR sample tubes. After heating for various intervals, the tubes were chilled with ice/water. The concentrations of the vinylcyclobutanes **1** or products **2** and **4** were determined from the ratios of suitable signals and the signal of the standard, in some cases also of ^{13}C-satellite bands of the solvent. Reactions were followed for more than 94% conversion. Between 12 and 26 points were measured. First-order rate constants and standard deviations were determined by nonlinear regression with the help of the computer program SPIRAL[26] and are given in Table 6, the free enthalpies of activation in Table 16. Eyring parameters and their statistical errors were calculated according to the algorithm of Denning by means of the computer program ACTPAR[27] and are listed in Table 9.

Kinetics in $LiClO_4$/Diethyl Ether: The concentrations of the vinylcyclobutanes **1** and the combined concentrations of the diastereomeric cyclohexenes **2** or dienoates **4** were determined by ^1H-NMR standard analysis in sealed tubes. The diastereomeric ratios of **2** and **4** could be evaluated only in the crude product mixture (≥94% material balance) in CCl_4 before chromatography. The kinetic systems of equations 1 and 2 were simulated with the program LARKIN[28] and optimized by iteration.

CAS Registry Numbers

(±)-**1a**: 127280-92-6 / (±)-**1b**: 127280-93-7 / (±)-**1c**: 127280-94-8 / (±)-**1d**: 127280-95-9 / (±)-**1e**: 127280-96-0 / (±)-**1f**: 127379-37-7 / (±)-**1g**: 127379-38-8 / (±)-**1h**: 127379-39-9 / (±)-**1i**: 127280-97-1 / (±)-**1k**: 127379-40-2 / (±)-**2a**: 127280-98-2 / (±)-**2b**: 127280-99-3 / (±)-**2c**: 127281-00-9 / (±)-**2d**: 127281-01-0 / (±)-**2e**: 127281-02-1 / (±)-**2f**: 127281-03-2 / **4a**: 2409-87-2 / **4b**: 35694-23-6 / **4c**: 122057-55-0 / **4d**: 127281-16-7 / **4e**: 689-89-4 / **4f**: 6932-46-3 / **4g**: 30361-31-0 / **4h**: 53892-48-1 / **8**: 127281-04-3 / **9a**: 127281-05-4 / **9b**: 127281-06-5 / **9c**: 127281-07-6 / **9d**: 127309-55-1 / **9e**: 127309-56-2 / **10c**: 127281-08-7 / **11a**: 127281-09-8 / **11b**: 127281-10-1 / **11c**: 127281-11-2 / **11d**: 127309-57-3 / **11e**: 127309-58-4 / **12a**: 127281-12-3 / **12c**: 127281-13-4 / **16b**$^+$ · ClO_4^-: 127281-15-6

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