Kinetics of Strain-Activated Intramolecular Diels-Alder Reactions Between Furan and Bicyclopropylidene as well as Methylenecyclopropane Moieties

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The intramolecular Diels-Alder reactions of the furans **1a**, **1b**, **3a** and **3b** in dichloromethane solution at pressures up to 3 kbar have been studied by quantitative on-line FT-IR spectroscopy. At identical pressure and temperature cyclization rates are significantly faster, by a factor of 8.1 and 6.8, for the **b**-type species of **1** and **3**, respectively. The activation enthalpies of the four cyclizations are very similar, between 78.5 ± 0.6 and 82.5 ± 2.7 kJ mol^{-1}. The activation volumes, $\Delta V_0^{\neq}$, are in the range -28.4 ± 1.3 (**1a**) to -40.8 ± 2.0 cm^3 mol^{-1} (**3b**). These data show that intramolecular Diels-Alder reactions are not necessarily associated with less negative activation volumes than intermolecular Diels-Alder reactions. The size of $\Delta V_0^{\neq}$, however, appears to be clearly correlated with the type and the position of substituents at the diene or dienophile moieties. Replacement of the H atom on the furan ring by the methoxy group turns $\Delta V_0^{\neq}$ more negative by 7.4 ± 2.9 cm^3 mol^{-1} for **1a** and **1b** and by 8.1 ± 2.0 cm^3 mol^{-1} for **3a** and **3b**. Varying the dienophile moiety from methylenecyclopropane to bicyclopropylidene lowers $\Delta V_0^{\neq}$ by about 3.5 cm^3 mol^{-1} between **1a** and **3a** and by about 5.0 cm^3 mol^{-1} between **1b** and **3b**, which demonstrates the larger steric hindrance due to the tetrasubstitution of the double bond. Comparing the effects on cyclization rate associated with having either one or two cyclopropane units at the dienophile double bond suggests that the rate enhancing influence of strain energy slightly overcompensates a reduction in rate that is expected to go with the increased steric hindrance due to the second cyclopropane unit.

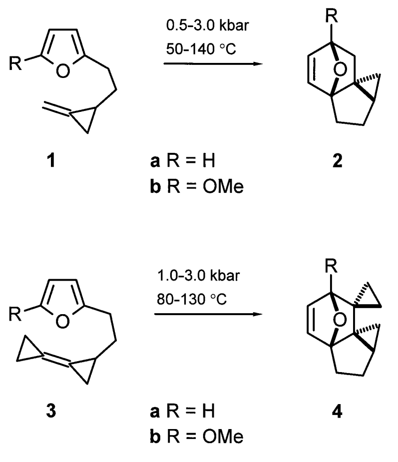
Introduction

The influence of high pressure on reaction rates and selectivities of Diels-Alder reactions has been studied primarily for intermolecular cycloadditions. Investigations on intramolecular Diels-Alder reactions up to high pressures are scarce[1]. Moreover, most of these studies have been concerned with systems containing electronically activated diene and/or dienophile moieties, except that Klärner et al. have thoroughly studied the intramolecular [4 + 2] cycloadditions of the non-activated trienes (*E*)-nona-1,3,8-triene and (*E*)-deca-1,3,9-triene and determined the activation volumes of these reactions[2]. It appeared rewarding to perform a systematic analysis into the kinetics of intramolecular Diels-Alder reactions with the dienophile being exclusively activated by strain energy. The furan components **1a**,**b** and **3a**,**b** depicted in Scheme 1 were used as model systems. The intramolecular cycloadditions are fully diastereoselective, yielding only the *exo* cycloadducts **2** and **4**, respectively.

The synthesis of the starting materials **1a**,**b**, **3a**,**b** and the full characterization of the products of their intramolecular cycloadditions have been reported elsewhere[3].

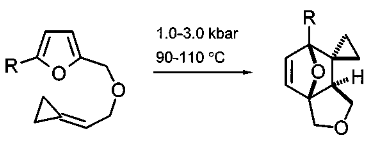
In a previous study[4] rate coefficients and activation parameters for the intramolecular Diels-Alder reaction of furan derivative **5** were measured. The trisubstituted methylenecyclopropane unit in **5** is tethered to the furan nucleus through an oxygen-containing bridge. The cyclization to **6** occurs with formation of a new five-membered ring.

Scheme 1



The present investigation on **1a**,**b** and **3a**,**b** addresses intramolecular cycloadditions, in which diene and dienophile are tethered via a CH_2CH_2 bridge. The 5′-methoxy substituent in **1b** and **3b** enhances the reactivity of the furan

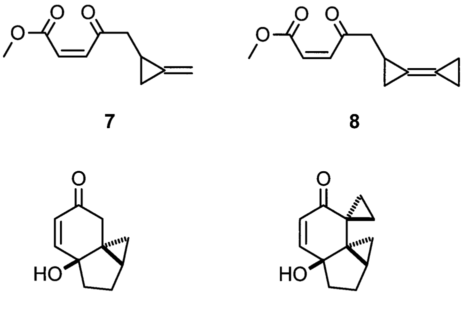
Scheme 2[1e]



5 **6**

nucleus. It appeared interesting to study whether the type of dienophile, **1** or **3**, influences the rate coefficients and the activation parameters to the same extent for R = H (type **a**) and R = OMe (type **b**). It needs to be mentioned that in the cycloadditions of **1a**,**b** and **3a**,**b** also products other than **2a**,**b** and **4a**,**b** are formed. For the starting materials of type **b**, **1b** and **3b**, at lower temperatures and moderately high pressures an oxidation reaction of the furan nucleus[5] (with small amounts of molecular oxygen that are present in the system) takes place leading to 1,4-dicarbonyl compounds **7** and **8**, respectively. To prove this, two experiments were repeated in a different cell which accomodates an inner cell made from a thick-walled Teflon® tube with two CaF_2 windows, with degassed solutions of the reactands. In these experiments the oxidation products **7**, **8** were not formed. It turned out to be rather difficult to completely remove oxygen when using the internal cell technique. Product samples containing **7** or **8** were not considered in the kinetic analysis. This limits the rate studies for **1b** and **3b** to temperatures above 70°C and pressures of at least 2000 bar, conditions under which the Diels-Alder reaction according to Scheme 1 is the predominant process. It must also be mentioned that **2a**,**b** and **4a**,**b** are not the final products of the cyclization of **1a**,**b** and **3a**,**b**. Especially the methoxy-substituted 7-oxanorbornene derivatives **2b**, **4b** are acid-sensitive and readily undergo opening of their oxygen bridges upon extended standing in dichloromethane solution to give tri- and tetracyclic cyclohexenone derivatives **9** and **10**, respectively[6]. These consecutive reactions, however, do not affect the kinetic analysis as the cycloaddition rate data are directly obtained from the spectroscopically measured time dependence of the concentration of **1a**,**b** and **3a**,**b**, respectively.

Scheme 3

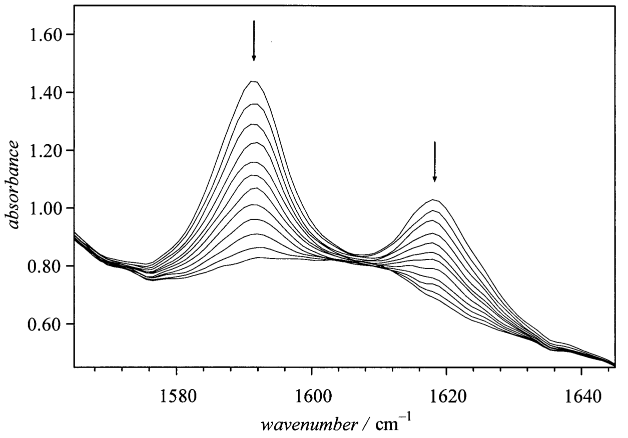


7 **8**

9 **10**

The cycloadditions have been followed by on-line quantitative infrared spectroscopy at high pressures up to 3 kbar. Figure 1 shows a spectral series recorded during the cyclization of **1b** at 2250 bar and 80°C over a time period of 5 h corresponding to 4.7 half lives. The vibrational modes under investigation at 1592 and 1619 cm^{-1} are the stretching vibrations of the C=C double bonds in the furan nucleus. The direction of spectroscopic change with time is indicated by the arrows.

Figure 1. Spectral series recorded during the cyclization of **1b** at 2250 bar and 80°C; a reaction time of 5 h corresponding to 4.7 half lives is covered; the arrows indicate the direction of spectral change with time



In dilute solutions at constant temperature and pressure Lambert-Beer's law is valid for the C=C stretching vibrations depicted in Figure 1. Thus the measured changes in integrated absorbances of these vibrations are proportional to the changes in concentration of the starting material as a function of reaction time. Different areas below the spectral bands have been integrated to achieve a reliable quantitative analysis, e.g. from 1580 to 1595 cm^{-1} or from 1580 to 1587.5 cm^{-1}. Fitting of an integrated absorbance vs. time profile to a first order rate expression by means of a least-squares procedure according to the Levenberg-Marquardt algorithm[7] yields the first-order rate coefficient k. As is illustrated in Figure 2 (in particular by plotting the residuals) for the cyclization of **3b** at 110°C and 2000 bar, the concentration (integrated absorbance) − time dependence is adequately represented by a first-order rate law up to 1800 s which corresponds to 4.5 half-lives under these reaction conditions.

Results and Discussion

The experimental first-order rate coefficients k of the intramolecular Diels-Alder reactions of **1a**, **1b**, **3a**, and **3b**, as obtained from the spectra via the Levenberg-Marquardt analysis (Figure 2), are summarized in Tables 1 to 4.

From the temperature dependence of k at constant pressure, activation enthalpies $\Delta H^{\neq}$ are derived according to eq. 1.

$$\Delta H^{\neq} = -\mathrm{R}(\mathrm{d} \ln k/\mathrm{d}\, T^{-1})_{\mathrm{p}} - \mathrm{R}T \qquad (1)$$

The $\Delta H^{\neq}$ values for the Diels-Alder reactions of **1a**, **1b**, **3a** and **3b** at 2000 bar are presented in Table 5. Also included in Table 5 are the activation entropies $\Delta S^{\neq}$ for the cycloadditions of **1a** to **3b**. They are calculated according to eq. 2.

Figure 2. Integrated absorbance vs. reaction time plot for the cyclization of **3b** at 110°C and 2 kbar; the difference between measured and fitted integrated absorbances is shown in the lower part of the figure

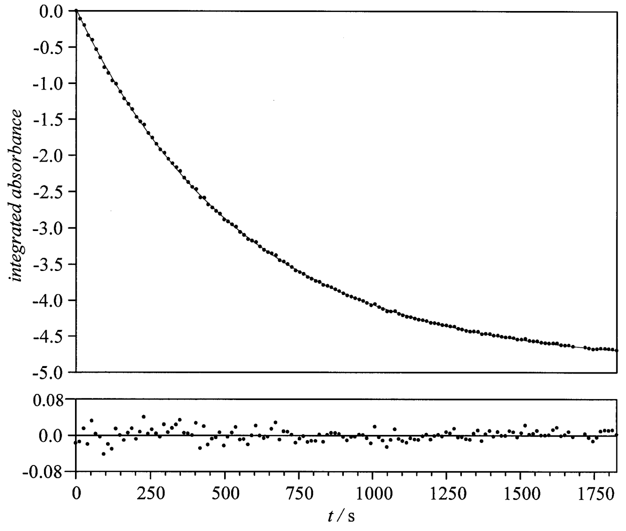


Table 1. Experimental first-order rate coefficients k for the intramolecular cycloaddition of **1a** in dichloromethane

p = 2000 bar		T = 110°C	
T [°C]	k [10^{-5} s^{-1}]	p [bar]	k [10^{-5} s^{-1}]
90	5.21	1000	10.7
100	9.40	1250	13.8
110	19.1	1500	13.7
120	38.0	1750	17.5
130	74.0	2000	19.1
140	134	2250	22.5
–	–	2500	24.6
–	–	2750	26.6
–	–	3000	28.4

Table 2. Experimental first-order rate coefficients k for the reaction of **1b** in dichloromethane

p = 2000 bar		T = 80°C	
T [°C]	k [10^{-5} s^{-1}]	p [bar]	k [10^{-5} s^{-1}]
50	2.04	500	16.5
55	2.74	1000	16.1
60	4.63	1250	16.1
65	5.74	1500	15.7
70	7.64	1750	17.2
80	16.9	2000	16.9
90	38.7	2250	20.4
100	76.6	2500	22.0
110	149	2750	24.5
–	–	3000	26.7

$$\Delta S^{\neq} = \mathrm{R}\,[A - \ln(k_{\mathrm{B}}\,T\,/\,h) - 1] \qquad (2)$$

where A is the intercept with the y axis of the ln k vs. T^{-1} (Arrhenius) plot; k_{B} and h are the Boltzmann constant and Planck constant, respectively.

Table 3. Experimental first-order rate coefficients k for the intramolecular cycloaddition of **3a** in dichloromethane

p = 2000 bar		T = 110°C	
T [°C]	k [10^{-5} s^{-1}]	p [bar]	k [10^{-5} s^{-1}]
80	3.02	1000	18.1
90	5.41	1250	19.6
100	13.3	1500	24.8
110	27.5	1750	28.4
120	50.0	2000	27.5
130	103	2250	33.8
–	–	2500	36.4
–	–	2750	36.7
–	–	3000	37.7

Table 4. Experimental first-order rate coefficients k for the reaction of **3b** in dichloromethane

p = 2000 bar		T = 80°C	
T [°C]	k [10^{-5} s^{-1}]	p [bar]	k [10^{-5} s^{-1}]
50	3.10	500	18.9
55	3.75	1000	18.4
60	6.47	1250	18.2
65	6.81	1500	19.2
70	9.50	1750	20.8
80	20.7	2000	20.7
90	46.1	2250	24.9
100	89.8	2500	27.4
110	177	2750	30.0
–	–	3000	33.3

Inspection of the entries for $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in Table 5 tells that substitution at either the diene or dienophile part has no significant influence on both quantities. The activation enthalpies are almost identical. The activation entropy turns out to be less negative for cycloadditions of **b**-type components. Reactions where the H atom on the furan ring has been replaced by a methoxy group are thus associated with a larger pre-exponential factor. In comparing individual $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values it should be recalled that both quantities are highly correlated: $\Delta H^{\neq}$ is determined from the slope and $\Delta S^{\neq}$ from the intercept with the ordinate of one and the same Arrhenius line fitted to a data set at constant pressure.

Table 5. Activation parameters and experimental rate coefficients k_{r} at 100°C and 2 kbar for the intramolecular cycloadditions of **1a**, **1b**, **3a** and **3b**

Compound	$k_{\mathrm{r}}^{[a]}$ [10^{-5} s^{-1}]	$\Delta H^{\neq [b]}$ [kJ mol^{-1}]	$\Delta S^{\neq [b]}$ [J mol^{-1} K^{-1}]	$\Delta V_0^{\neq}$ [cm^3 mol^{-1}]
1a	9.40	80.2 ± 1.5	−92 ± 4	−28.4 ± 1.3 (110°C)
3a	13.0	82.5 ± 2.7	−84 ± 7	−31.9 ± 1.9 (110°C)
1b	76.6	80.3 ± 0.6	−75 ± 2	−35.8 ± 2.9 (80°C)
3b	89.8	78.5 ± 0.6	−78 ± 2	−40.8 ± 2.0 (80°C)

[a] 100°C and 2000 bar. – [b] 2000 bar.

The close similarity of $\Delta H^{\neq}$ values for the reactions of **1a**, **1b**, **3a** and **3b** in CH_2Cl_2 solution at 2000 bar is also evident form the Arrhenius lines in Figure 3. The open symbols for the reactions of **1b** and **3b** at temperatures below 70°C refer to situations where the above-mentioned transformation with molecular oxygen to **7a**,**b** interferes with the Diels-Alder process. These data (open symbols) are not included in the kinetic analysis. Figure 3 clearly demonstrates that cycloadditions of **b**-type starting materials (**1b**, **3b**) are significantly faster than the corresponding **1a** and **3a** cycloadditions. To allow for a quantitative comparison, first-order rate coefficients k_r for a reference reaction condition (100 °C, 2000 bar) have been included in Table 5. These data show that the methoxy substituent enhances the rate in the methylenecyclopropane system **1** by a factor of 8.1 (going from **1a** to **1b**) and by a factor of 6.8 in the bicyclopropylidene system (going from **3a** to **3b**). The k_r values in Table 5 also reveal that the second cyclopropane ring leads to a slight increase in rate, by about 40% for the **3a** vs. **1a** reactions and by about 20% for the **3b** vs. **1b** cycloadditions. These results suggest that the larger steric hindrance associated with the second cyclopropane ring attached at the dienophilic double bond is slightly overcompensated by the rate enhancement originating from the release in strain energy of this additional methylenecyclopropane unit. Partial compensation of the contributions from strain energy and from steric hindrance may also be the reason why activation enhalpies for the reaction of dienophilic moieties with strain release from either one or two cyclopropane rings are close to each other (Table 5). It should also be noted that the activation enthalpies of 78.5 to 82.5 kJ mol^{-1} are fairly large as compared to electronically activated systems where values between 40 and 60 kJ mol^{-1} are frequently found. On the other hand, the activation enthalpies for the cyclization of **1** and **3** are considerably smaller than those for the intramolecular [4 + 2] cycloadditions of (*E*)-1,3,8-nonatriene to give *cis*- and *trans*-bicyclo[4.3.0]non-2-ene[2]. It must be primarily due to the CH_2CH_2 bridge between diene and dienophile (which reduces the entropy penalty) that the intramolecular cycloadditions in the systems **1** and **3** take place at reasonable rates. The rate for an intermolecular Diels-Alder reaction between functional groups as in **1** and **3** may be estimated by using a typical value of activation entropy for an intermolecular cycloaddition ($\Delta S^{\neq} = -145$ J K^{-1} mol^{-1}) in combination with the activation enthalpies from Table 5. An estimate yields fairly low cycloaddition rates, e.g. $k_r = 3.8 \times 10^{-7}$ s^{-1}, for an intermolecular reaction between a furan and a bicyclopropylidene derivate as in system **3a**. This k value corresponds to a reaction half-life of 21 d, which provides some explanation why intermolecular Diels-Alder reactions between furans and bicyclopropylidene corresponding to system **3** have not yet been successful.

Information about steric hindrance should be available from an inspection of cyclization rates measured as a function of pressure. The ln k vs. p data for the Diels-Alder reactions of **1a** and **3a**, both at 110 °C, are presented in Figure 4. Corresponding data for the pressure dependence of the **1b** and **3b** cyclizations at 80 °C are presented in Figure 5. The pressure range in Figure 5 is rather limited because of contributions from the oxidative side reactions to **7a**,**b** which pose problems toward quantitative kinetic analysis at pressures below 2 kbar.

Figure 3. Temperature dependence of the experimental rate coefficients k for the cycloaddition reaction of **1a**, **1b**, **3a** and **3b** at 2 kbar

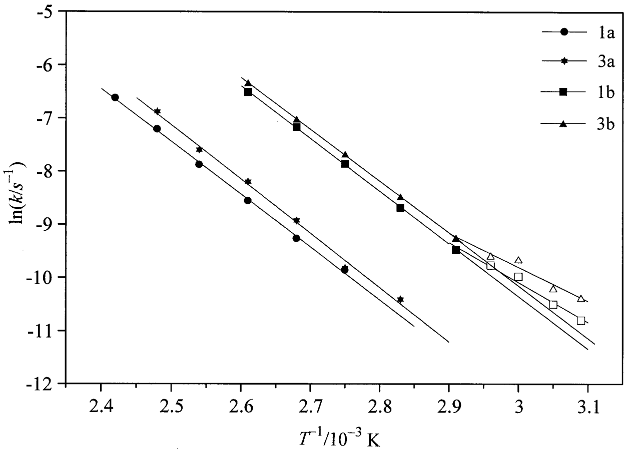


Figure 4. Pressure dependence of the experimental rate coefficients k for the cycloaddition reaction of **1a** and **3a** at 110 °C

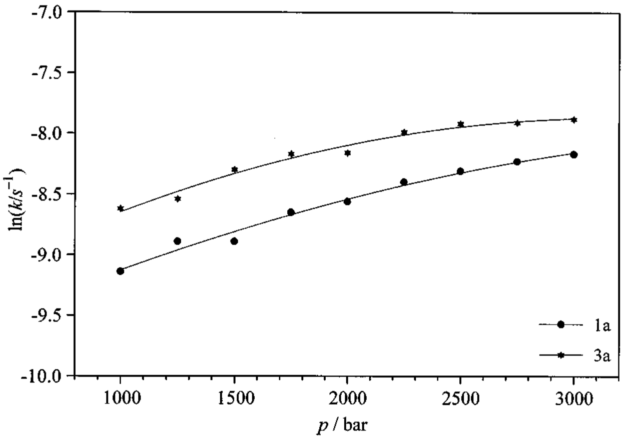
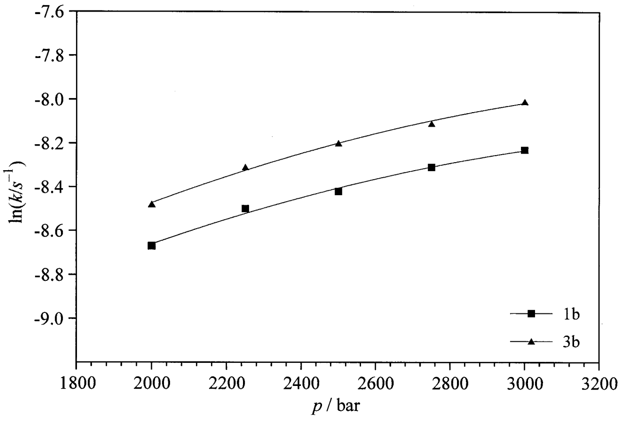


Figure 5. Pressure dependence of the experimental rate coefficients k for the cycloaddition reaction of **1b** and **3b** at 80 °C



The ln k vs. p relations are slightly curved. According to the methods described by Asano et al.[8] activation volumes are derived by fitting of eq. 3 and of eq. 5 to k values measured at constant temperature. From the fitted parameters the activation volume referring to ambient pressure, $\Delta V_0^{\neq}$, is obtained via eqs. 4 and 6, respectively. k_0 is derived from a parabolic fit of the ln k vs. p data prior to the analysis via eqs. 3 and 5.

$$\ln (k/k_0) = a_I p + [b_I p/(1+c_I p)] \quad (3)$$

$$\Delta V_0^{\neq} = -(a_I+b_I)RT \quad (4)$$

$$\ln (k/k_0) = a_{II} p + b_{II} \ln (1 + c_{II} p) \quad (5)$$

$$\Delta V_0^{\neq} = -(a_{II} + b_{II} c_{II})RT \quad (6)$$

Both procedures, the estimate of $\Delta V_0^{\neq}$ via eqs.3 and 5, yield numbers that are identical within experimental uncertainty. The method of El′yanov et al.[9] which has been used extensively toward $\Delta V_0^{\neq}$ analysis of intermolecular Diels-Alder reactions could only be applied after adjustment of the coefficients α and β to the particular **1a**,**b**, **3a**,**b** systems. With this modification, the El′yanov procedure gave $\Delta V_0^{\neq}$ values in full agreement with the data from the analysis using eqs. 3 to 6.

The activation volumes are also given in Table 5. The numbers refer to different temperatures, 80 and 110°C. Investigations by Niklaus[10] into the temperature dependence of activation volumes for the intramolecular Diels-Alder reaction of a benzylidenebarbituric acid derivate indicate that such a dependence, if it occurs at all, should be rather weak. Accordingly, a difference in reaction temperature of 30°C, as in Table 5, is considered to be negligible for the subsequent analysis. Moreover, even a substantial temperature dependence of activation volume, e.g. as suggested for intermolecular Diels-Alder reactions by El′yanov et al.[9] would not significantly influence the relative sizes of the $\Delta V_0^{\neq}$ data in Table 5.

The numbers in Table 5 are typical for activation volumes of Diels-Alder reactions[11]. The data, in particular those for the cyclizations of **1b** and **3b**, provide no indication for activation volumes of intramolecular Diels-Alder reactions being generally less negative than those of intermolecular reactions[12]. On the other hand, the activation volume seems to depend significantly on the type and on the location of the substituents at the diene and dienophile moieties.

The activation volumes of the type-**a** intramolecular cyclizations (**1a** and **3a**) are clearly above (smaller negative values) the activation volumes of the type-**b** cyclizations. The differences in $\Delta V_0^{\neq}$ between **1a** and **1b** and between **3a** and **3b** are 7.4 ± 2.9 cm^3 mol^{-1} and 8.1 ± 2.0 cm^3 mol^{-1}, respectively. The lowering of $\Delta V_0^{\neq}$ upon replacing the H atom at the 5-position of the furan nucleus by the methoxy substituent may be understood by two effects operating in parallel: (1) Substitution at the furan nucleus polarizes the transition state and thus reduces $\Delta V_0^{\neq}$ because of electrostriction[12] in the polar solvent. (2) Stronger steric hindrance is known to be associated with a larger negative activation volume. Thus type-**b** cycloadditions are expected to show lower $\Delta V_0^{\neq}$. To sort out the relative importance of these two effects, further kinetic studies should be made at systematic variation of solvent polarity.

The changes in activation volumes upon replacing the methylenecyclopropane unit by the bicyclopropylidene unit are very similar for type-**a** and type-**b** systems. The activation volume is smaller in cyclizations with two cyclopropane rings at the dienophile moiety, by about 3.5 cm^3 mol^{-1} for **1a** and **3a** and by about 5.0 cm^3 mol^{-1} for **1b** and **3b**. This observation is fully consistent with the expectation of a more crowded transition state for a tetrasubstituted dienophile than for a disubstituted dienophile.

Experimental Section

The preparation of the model compounds **1a**,**b**, **3a**,**b**, and the characterization of their products (Scheme 1) has previously been described[3]. All substrates were freshly purified prior to the kinetic experiments.

An optical high-pressure cell equipped with windows from polycrystalline silicon was used. The dichloromethane solution of each substrate was contained within an internal Teflon® cell positioned between the windows of the high-pressure cell. The experimental set-up and the procedures of preparing, filling and sealing the internal cell are described in detail elsewhere[14]. The initial substrate concentrations were chosen between 0.02 and 0.1 mol (kg solution)$^{-1}$ depending on the absorption intensity of the vibrational mode under investigation. The decadic absorbance should not exceed $A = 1.8$ in order to stay within the linear range of the DTGS detector used with the Bruker IFS 88 FT spectrometer. This limitation must be taken into account to ensure reliable quantitative spectroscopic analysis. Pressures were determined to better than ± 10 bar. The uncertainty in temperature was below ± 0.5 K.

Methyl (Z)-6-(2′-Methylenecyclopropyl)-4-oxohex-2-enoate (**7**): To a suspension of 1.0 g (4.9 mmol) of pyridinium chlorochromate (PCC) in 20 ml of dichloromethane (DCM), was slowly added by syringe a solution of 178 mg (1.0 mmol) of the furan derivative **1b** in 5 ml of DCM at room temp. After 30 min, 30 ml of diethyl ether was added to precipitate the excess of PCC, and the mixture was filtered through silica gel and concentrated to yield 180 mg of crude product mixture. The product was purified by chromatography on silica gel (eluent hexane/ether, 8:2) to yield 98 mg (49%) of **7**. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.70−0.80 (m, 1 H), 1.24 (m, J = 7.5 Hz, 1 H), 1.40−1.50 (m, 1 H), 1.55−1.85 (m, 2 H), 2.71 (t, J = 7.5 Hz, 2 H), 3.74 (s, 3 H), 5.34 (br. s, 1 H), 5.40 (br. s, 1 H), 6.03 (d, J = 12.0 Hz, 1 H), 6.50 (d, J = 12.0 Hz, 1 H). − IR (film): ṽ = 2953 cm^{-1}, 1728, 1700, 1559, 1540, 1506, 1437, 1388, 1226, 1111, 999, 889, 814. − EI-MS; *m/z* (%): 194 [M^+], 179 (5), 147 (7), 145 (8), 134 (12), 114 (18), 113 (100).

Methyl (Z)-6-(2′-Bicyclopropylidenyl)-4-oxohex-2-enoate (**8**): According to the procedure for the preparation of **7**, 206 mg (1.0 mmol) of the furan derivative **2b** gave 105 mg (47%) of **8**. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.85−0.95 (m, 1 H), 1.10−1.20 (m, 4 H), 1.30−1.40 (m, 1 H), 1.55−1.65 (m, 1 H), 1.82−1.92 (m, 2 H), 2.75 (t, J = 7.5 Hz, 2 H), 3.71 (s, 3 H), 6.05 (d, J = 12.0 Hz, 1 H), 6.50 (d, J = 12.0 Hz, 1 H).

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