The Effect of Pressure on Retro Diels–Alder Reactions

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The activation and reaction volumes ($\Delta V^{\neq}/\Delta V$) were determined for the retro Diels–Alder reactions of the parent dihydrobarrelene **1a**, its 2-cyano derivative **1b**, the *exo* and *endo* Diels–Alder adducts of maleic anhydride to naphthalene *exo*-, *endo*-**4**, and the *exo* and *endo* Diels–Alder adducts of *N*-phenylmaleic imide to 6,6-dimethylfulvene *exo*-, *endo*-**8** from the pressure dependence of the rate constants and the partial molar volumes (V) of reactants and products at various temperatures. The cleavage of *exo*-**4**, *endo*-**4**, and *exo*-**8** are slightly accelerated by pressure showing negative volumes of activation ($\Delta V^{\neq} < 0$) whereas the others are slightly retarded ($\Delta V^{\neq} > 0$). From the analysis of the volume data including the van der Waals volumes (V_w) one can conclude that the packing coefficients of the pericyclic transition states are equal to or even larger than those of the corresponding Diels–Alder adducts. This finding may be explained with the restriction of the degrees of freedom in the transition states leading to a contraction of the expansion volume.

Many Diels−Alder reactions show a powerful pressure-induced acceleration which is often turned to good synthetic purposes.[1][2] The activation volumes $\Delta V^{\neq}$ resulting from the pressure dependence of the rate constants are usually highly negative ($\Delta V^{\neq} \approx -25$ to -45 cm^{3}mol^{-1}), sometimes even more negative than the corresponding reaction volume ΔV so that the $\Delta V^{\neq}/\Delta V$ ratio is close to or even larger than unity ($\Theta = \Delta V^{\neq}/\Delta V \geq 1$).[3]

Within the scope of the transition-state theory, activation volumes can be considered to be a measure of the relative partial molar volume of the transition states [$\Delta V^{\neq} = V^{\neq}(\mathrm{TS}) - \Sigma V(\mathrm{reactants})$]. Accordingly, the molar volumes of transition states of many Diels−Alder reactions are approximately equal to or even smaller than those of the corresponding cycloadducts. These surprising results could be confirmed by two independent studies. In the Diels−Alder reactions of furan with acrylonitrile[4] and in that of *N*-benzoylpyrrole with *N*-phenylmaleic imide[5] the ratio $\Delta V^{\neq}/\Delta V$ was found to be larger than unity (Θ = 1.06 and 1.37, respectively). The cycloadducts isolated from both reactions undergo smooth retro Diels−Alder reactions showing negative volumes of activation in agreement with the value $\Theta > 1$ determined for the forward reactions.

The observation that the transition-state volume in several Diels−Alder reactions is smaller than the product volume, is surprising and not well understood. This finding seems to be contradictory to the generally accepted relation between molecular structure and its volume. In the transition state the new bonds between diene and dienophile are only partially formed. According to quantum-mechanical calculations[6] the lengths of the newly forming σ bonds in pericyclic transition states are in the range between 2.1 and 2.3 Å.

The intrinsic molar volumes, the so-called van der Waals volumes, V_W, calculated for the pericyclic transition structures of Diels−Alder reactions by the use of the structural parameters obtained from quantum-mechanical calculations[6] and the van der Waals radii of the different types of atoms derived from X-ray data are generally larger than those calculated analogously for the corresponding cycloadducts.[3g,7] Grieger and Eckert[8] considered two explanations of the ratio $\Theta > 1$ in the Diels−Alder reaction of isoprene as diene with maleic anhydride as dienophile: a larger dipole moment of the transition state or secondary orbital interactions[9] from which the secondary orbital interactions can only occur in *endo* Diels−Alder reactions. The finding that the difference between the activation volumes of many *endo* and *exo* Diels−Alder reactions is small ($\Delta\Delta V^{\neq} > 1-2$ cm^{3}mol^{-1}),[1e] seems to rule out that secondary orbital interactions are important and induce a larger contraction of the volume of the *endo* transition state.

In order to gain further insight into this remarkable effect, we investigated the volume profiles of retro Diels−Alder reactions of several dihydrobarrelene and 7-isopropylidenenorbornene systems starting from the nonpolar parent hydrocarbon **1a** going to the systems **1b**, *endo*-, *exo*-**4**, and *endo*-, *exo*-**8** substituted by polar groups in different positions.

The retro Diels−Alder reaction of dihydrobarrelene **1a** leading to benzene **3a** and ethene is decelerated by pressure and its activation volume was determined from the pressure dependence of the rate constants at 105.3 °C to be slightly positive (Scheme 1). The partial molar volumes of **1a** and benzene and, hence, the volume of reaction at 105.3 °C, the temperature of reaction, were obtained from the temperature- and concentration-dependent density measurement of **1a** and benzene, respectively, dissolved in *n*-hexane. The partial molar volume of gaseous ethene was extrapolated by means of Exner increments[10] and by the use of the temperature coefficient κ_0 determined for benzene (Scheme 1).

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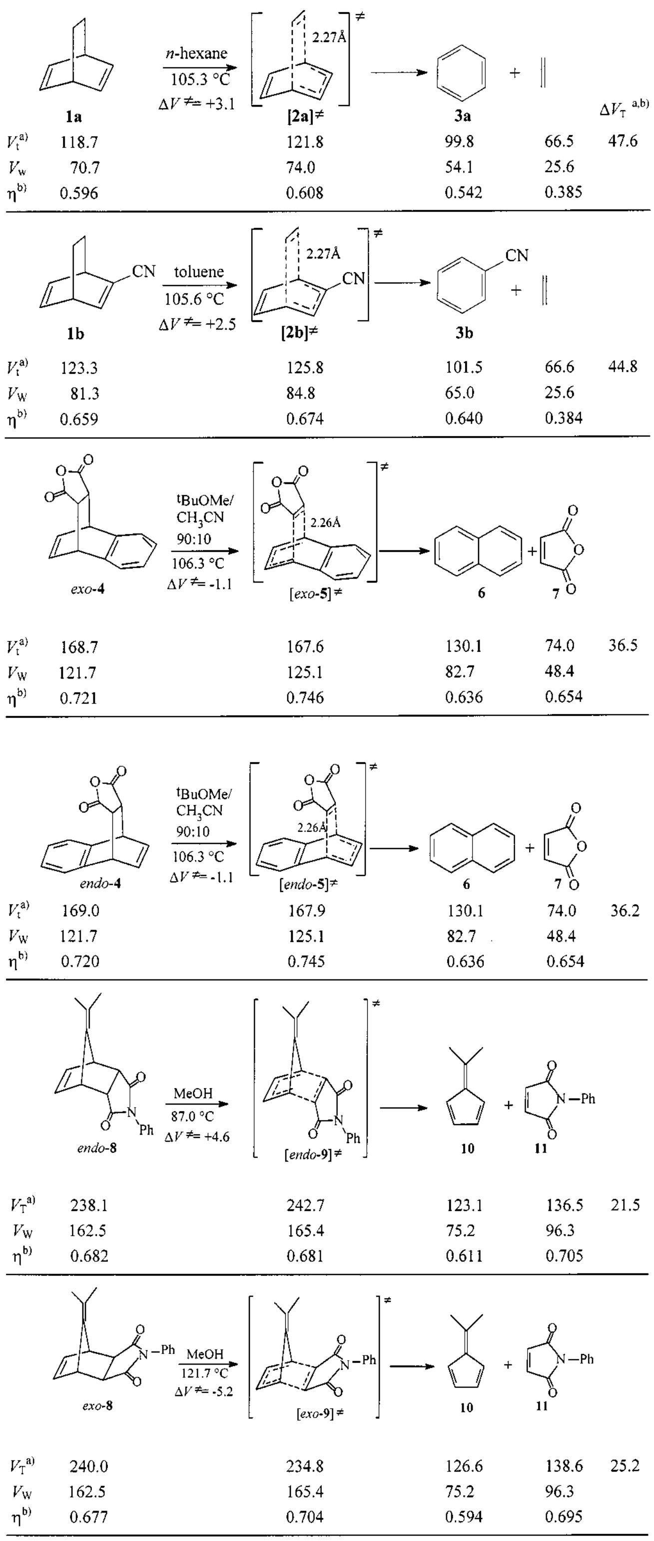

	1a	**[2a]≠**	**3a**		ΔV_T $^{a,b)}$
V_t $^{a)}$	118.7	121.8	99.8	66.5	47.6
V_w	70.7	74.0	54.1	25.6	
η $^{b)}$	0.596	0.608	0.542	0.385	

	1b	**[2b]≠**	**3b**		
V_t $^{a)}$	123.3	125.8	101.5	66.6	44.8
V_W	81.3	84.8	65.0	25.6	
η $^{b)}$	0.659	0.674	0.640	0.384	

	exo-**4**	[*exo*-**5**]≠	**6**	**7**	
V_t $^{a)}$	168.7	167.6	130.1	74.0	36.5
V_W	121.7	125.1	82.7	48.4	
η $^{b)}$	0.721	0.746	0.636	0.654	

	endo-**4**	[*endo*-**5**]≠	**6**	**7**	
V_t $^{a)}$	169.0	167.9	130.1	74.0	36.2
V_W	121.7	125.1	82.7	48.4	
η $^{b)}$	0.720	0.745	0.636	0.654	

	endo-**8**	[*endo*-**9**]≠	**10**	**11**	
V_T $^{a)}$	238.1	242.7	123.1	136.5	21.5
V_W	162.5	165.4	75.2	96.3	
η $^{b)}$	0.682	0.681	0.611	0.705	

	exo-**8**	[*exo*-**9**]≠	**10**	**11**	
V_T $^{a)}$	240.0	234.8	126.6	138.6	25.2
V_W	162.5	165.4	75.2	96.3	
η $^{b)}$	0.677	0.704	0.594	0.695	

Scheme 1. Activation volumes ($\Delta V^{\neq}$), partial molar volumes V_T determined experimentally and van der Waals volumes V_w calculated by means of the program MOLVOL[7e] which uses the cartesian coordinates of the ground and transition structures obtained from force-field and quantum-mechanical ab initio calculations, respectively; all volumes in cm^3mol^{-1}; $^{a)}$ extrapolated from the temperature dependence of V between T_0 = 20°C and T = 70°C by the use of the El'yanov equation $V_T = V_0 \cdot [1 + \kappa_0 \cdot (T - T_0)]$; V_0 [cm^3 mol^{-1}]/$\kappa_0 \cdot 10^4$ [K^{-1}]: 110.6/8.86 (**1a**); 90.0/13.0 (**3a**); 113.4/10.2 (**1b**); 100.3/1.37 (**3b**); 164.2/3.19 (*exo*-**4**); 164.3/3.31 (*endo*-**4**); 122.9/6.83 (**6**); 69.3/7.88 (**7**), 227.4/7.04 (*endo*-**8**); 230.0/4.28 (*exo*-**8**); 116.2/8.83 (**10**); 132.3/4.69 (**11**); $^{b)}$ $\eta = V_W/V_T$

From these data, the complete volume profile of this reaction (Figure 1) can be constructed. The ratio of activation volume to reaction volume for the experimentally inaccessible Diels–Alder reaction of benzene with ethene is calculated to be $\Theta = \Delta V^{\neq}/\Delta V = 0.94$ and, hence, only slightly smaller than unity as found for many other Diels–Alder reactions, too. The packing coefficient η of the pericyclic transition state [**2a**]$^{\neq}$ calculated from the ratio of its van der Waals volume to its partial molar volume, $\eta = V_W/V$ = 0.608, turned out to be approximately equal to or even a little larger than that of the cycloadduct **1a**, η = 0.596.

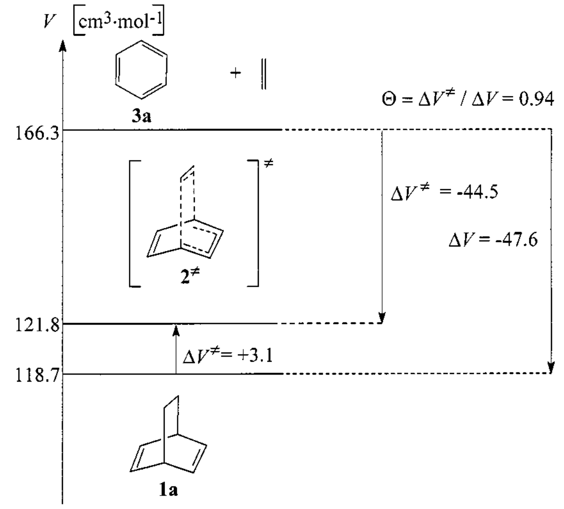

Figure 1. Volume profile of the retro Diels–Alder reaction of dihydrobarrelene (**1a**) leading to benzene (**3a**) and ethene

Similar results were obtained for the reaction of 2-cyanodihydrobarrelene **1b** included in Scheme 1. Again, the packing coefficient of the pericyclic transition state was found to be slightly larger than that of the corresponding cycloadduct **1b**. The retro Diels–Alder reactions of *endo*-**4** and *exo*-**4** leading both to naphthalene **6** and maleic anhydride (**7**; MA), however, are slightly accelerated by pressure showing negative volumes of activation (Scheme 1). Again, the packing coefficients are calculated to be larger for the pericyclic transition state than for the corresponding cycloadducts.

The effect of pressure on the Diels–Alder reaction of naphthalene **6** with MA (**7**) leading to a mixture of *endo*-**4** and *exo*-**4** is worth mentioning. At 100°C, this reaction, which was reported by Plieninger et al.[11] to be the best method for the synthesis of *endo*-**4** and *exo*-**4**, occurs in reasonable yields only at pressures higher than 7 kbar in relatively concentrated solutions. In dilute solutions the reaction stops at a relatively low pressure-dependent conversion of naphthalene (**6**; Table 1). The ratio [**6**]/[*endo*-**4**]/[*exo*-**4**] measured in relatively dilute solutions of the reactants obviously represents the equilibrium mixture at different pressures. The solubility of *endo*-**4** and *exo*-**4** is certainly pressure-dependent, too, so that these cycloadducts precipitate from concentrated solutions at high pressure. The precipitation causes a shift of the equilibrium toward the cycloadducts. Under optimized conditions of reaction ($[\mathbf{6}]_0$ =

$[7]_0$ = 1.1 M, in $CHCl_3$ at 100°C, 12 kbar, 48 h), *endo*-**4** and *exo*-**4** can be prepared in a yield of 94%.

Table 1. Pressure dependence of the ratio of [**6**]/[*exo*-**4**]/[*endo*-**4**] in the Diels–Alder reaction of naphthalene (**6**) with MA (**7**); $[6]_0 = [7]_0$ = 50 mM in $CDCl_3$ at T = 100°C, time of reaction t = 22 h

p [kbar]	**6** (%)	*exo*-**4** (%)	*endo*-**4** (%)	*exo*-**4**/*endo*-**4**
7.0	96.8	2.1	1.1	64:36
8.0	94.5	3.7	1.9	65:35
9.0	92.8	4.8	2.5	66:34
10.0	88.7	7.5	3.8	66:34
11.0	75.1	16.5	8.5	66:34
12.0	66.7	17.4	15.91	52:48[a]

[a] At 12 kbar *exo*-**4** and *endo*-**4** already precipitate partially. Therefore, the ratio analyzed by ^{1}H NMR of the solution does not represent the actual amount of the reactants and products.

The effect of pressure on the retro Diels–Alder reactions of *endo*-**8** and *exo*-**8** leading both to dimethylfulvene **10** and *N*-phenylmaleic imide (**11**) are clear-cut examples which show that secondary orbital interactions are not important for the finding of negative volumes of activation in retro Diels–Alder reactions. The reaction of *endo*-**8** is decelerated by pressure, showing $\Delta V^{\neq} > 0$ whereas the reaction of *exo*-**8** is accelerated by pressure, showing $\Delta V^{\neq} < 0$ (Scheme 1). In the case of $[endo\text{-}\mathbf{9}]^{\neq}$ the packing coefficient is calculated to be equal to that of *endo*-**8** and in the case of $[exo\text{-}\mathbf{9}]^{\neq}$ larger than that of *exo*-**8**.

The following conclusions can be drawn from these results. The packing of the entire ensemble consisting of solute and solvent molecules and its reorganization during the course of the reaction, and not the changes of the intrinsic molecular volumes of the reactants to the products during the course of reaction, are most important for the magnitude of activation and reaction volumes. The packing coefficients of the pericyclic transition states resemble those of the corresponding cycloadducts as already assumed for the explanation of the different activation volumes of pericyclic and stepwise cycloadditions involving diradical intermediates.[12] In the retro Diels–Alder reactions showing $\Delta V^{\neq} < 0$, the packing coefficients of transition states are calculated to be significantly larger than those of the corresponding cycloadducts. This has been found particularly in the relatively polar systems bearing cyclic anhydride or imide functions. In these cases, the size of the activation volumes obviously depend not only on the effective packing around the transition states, probably caused by the restriction of vibrations and rotations, but also on the transition-state polarization enhanced by the polar groups. Blake and Jorgensen have assumed similar effects to explain the acceleration of the Diels–Alder reaction of 1,3-cyclopentadiene with methyl vinyl ketone in water.[13]

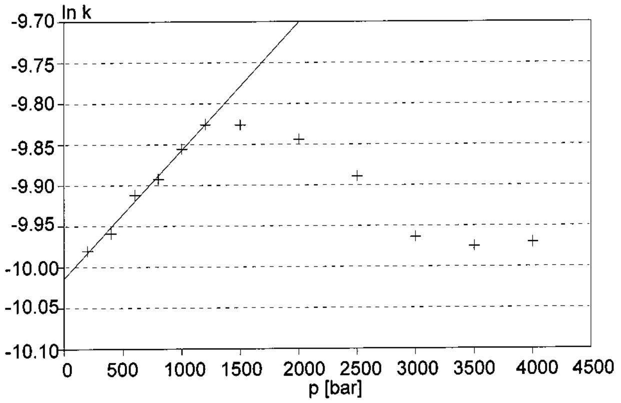

Figure 2. The pressure dependence of the rate constants of the retro Diels–Alder reaction *exo*-**8** → **10** + **11** at 87.0°C in methanol

The retro Diels–Alder reaction *exo*-**8** → **10** + **11** exhibits an unusual pressure dependence (Figure 2) comparable to that observed by Asano et al. for the *syn* → *anti* isomerization in azobenzenes and *N*-benzylideneanilines.[14] The reaction *exo*-**8** → **10** + **11** is accelerated by raising the pressure from 1 to ca. 1200 bar (the activation volume given in Scheme 1 is calculated from these values), whereas the rate of reaction is decreased at pressures higher than 1500 bar up to 3000 bar and then remains almost constant between 3000 and 4000 bar. A similar but less pronounced pressure dependence is also observed for the reaction *exo*-**4** → **6** + **7**. According to preliminary thermolyses of *exo*-**8** in different solvents at different pressures, there is no relationship between the pressure-dependence of the rate constant and the solvent viscosity, contrary to the results obtained by Asano et al.[14] and Troe et al.[15] for their systems. Further investigations are required for these remarkable effects to be elucidated.

Experimental Section

^{1}H NMR, ^{13}C NMR, DEPT, H,H COSY, C,H COSY: Bruker AM-X 300 (^{1}H NMR: 300 MHz; ^{13}C NMR: 75 MHz); the residual protio solvent is used as internal standard; chemical shifts (δ) are reported relative to tetramethylsilane [δ(TMS) = 0]. – IR: Infrared spectrophotometer FTIR 1600 Series Spectrometer (Perkin–Elmer). – MS: VG ProSpec 3000 (Fisons Instruments, 70 eV). – Melting points are not corrected. – GC analyses are performed with a Hewlett Packard HP 5890 (FID) with a Shimadzu C-R6A integrator and a Carlo Erba Strumentatione (FID) with a Shimadzu C-R6A integrator (carrier gas: He); column A: fused silica OV17, 0.5 µm, 0.25 mm i.d. × 30 m; column B: fused silica RTX200, 1.0 µm, 0.32 mm i.d. × 30 m. Retention time is abbreviated as t_R. – HPLC analyses: Jasco PU-980 intelligent HPLC pump with Jasco DG-890–50 3-line degasser, Jasco LG-980–02 ternary gradient unit and Shimadzu SPD-6A UV spectrophotometric detector; integrations are performed with the program NINA 4.1 chromatographic system (Nuclear Interface); column C: analytical Spherisorp SW (Knauer), 3 µm, 4 × 125 mm; column D: analytical Hypersil-100 CN (Knauer), 3 µm, 4 × 125 mm; column E: analytical ODS-18 (Knauer), 3 µm, 4 × 125 mm. – Preparative high pressure experiments are carried out in a 14-kbar system containing a 100-mL vessel manufactured by A. Hofer Hochdrucktechnik GmbH, 45481 Mühlheim/Ruhr, the vessel is heated with an external thermostat (temperature accuracy: ± 1°C). – For pressure-dependent kinetic measurements, a 7-kbar vessel is heated by an external oil bath thermostated to ± 0.2°C and pressurized by a motor-driven press (Dieckers). In order to follow the time dependence of a reaction at elevated pressure, one exit of the vessel is connected to a valve equipped with a fine spindle which allows the release of a small sample (ca. 100 µL) from the pressur-

Table 2. Pressure dependence of the specific rate constants k of retro Diels−Alder reactions at different temperatures

p	200	300	400	500	600	700	800	1000	1200	1400	1500	1600	2000	2500	3000	3500	4000
Reaction (*T* [°C])	k [10^{-5}s^{-1}]																
1a → **3a** + **2** (105.3)			3.71 ± 0.02		3.73 ± 0.03		3.55 ± 0.03	3.61 ± 0.03			3.34 ± 0.03		3.21 ± 0.02		2.91 ± 0.03		
1b → **3b** + **2** (105.6)			3.09 ± 0.05		3.15 ± 0.15		3.04 ± 0.10	2.95 ± 0.04	3.01 ± 0.11		2.99 ± 0.11		2.81 ± 0.08		2.52 ± 0.03		
endo-**4** → **6** + **7** (106.3)	4.57 ± 0.05	4.60 ± 0.04	4.64 ± 0.07	4.58 ± 0.06	4.67 ± 0.05	4.69 ± 0.09	4.67 ± 0.06	4.73 ± 0.04	4.70 ± 0.05	4.81 ± 0.05		4.76 ± 0.07	4.75 ± 0.13	4.79 ± 0.05	4.82 ± 0.08	4.80 ± 0.06	4.76 ± 0.17
exo-**4** → **6** + **7** (106.3)	4.30 ± 0.03		4.30 ± 0.12	4.24 ± 0.05		4.40 ± 0.08	4.32 ± 0.04	4.41 ± 0.03			4.47 ± 0.04		4.27 ± 0.04	4.13 ± 0.07	3.91 ± 0.02		3.76 ± 0.13
endo-**8** → **10** + **11** (87.0)	4.77 ± 0.02	4.77 ± 0.05	4.73 ± 0.07	4.44 ± 0.04			4.37 ± 0.09		4.12 ± 0.07			3.86 ± 0.13	3.41 ± 0.04	2.62 ± 0.04	2.43 ± 0.06	1.89 ± 0.11	
exo-**8** → **10** + **11** (121.7)	4.63 ± 0.13		4.73 ± 0.11		4.96 ± 0.15		5.06 ± 0.07	5.25 ± 0.11	5.41 ± 0.08		5.40 ± 0.06		5.31 ± 0.13	5.07 ± 0.17	4.71 ± 0.10	4.65 ± 0.22	4.68 ± 0.23

ized reaction mixture (8−10 mL). The decrease of pressure during the release of the sample is constantly monitored by the use of a pressure transducer and corrected by a computer-driven control appliance. The analysis of the composition of products in the released sample is performed by GC or HPLC. − For density measurements a densimeter DMA 48 (Chempro) is used. − Dihydrobarrelene (**1a**) was prepared according to the literature[16] and purified by preparative GC [aerograph P 90 with WLD (Varian), column: 2.5 m 1/4 inch column packed with 20% Carbowax on Chromosorb P, carrier gas: He (100 ml·min^{-1}), 70°C, t_R = 10 min]. 2-Cyanodihydrobarrelene (**1b**) was prepared as previously described.[17]

***exo*- and *endo*-2,3-Benzobicyclo[2.2.2]octa-2,5-diene-7,8-dicarboxylic Anhydride (*exo*- and *endo*-4):** A solution of naphthalene (**6**; 1.13 g, 8.83 mmol) and maleic anhydride (**7**; 0.86 g, 8.78 mmol) in 8 mL of chloroform was sealed in a PTFE tube and thermolyzed for 48 h at 100°C and 12 kbar (conversion: 94%; ratio of *exo*-**4**/*endo*-**4** = 66:34 determined by ^{1}H NMR, CDCl$_3$ of the crude reaction mixture after removal of the solvent). The mixture was separated in portions of 100 mg by column chromatography (30 g SiO$_2$; cyclohexane/ethyl acetate, 6:1; UV detection 254 nm; fraction 1: **6**; fraction 2: *exo*-**4**; fraction 3: *endo*-**4**) The separated adducts were further purified by recrystallization from CHCl$_3$/cyclohexane, 1:1. Yields: *exo*-**4** (0.9 g 45%), m.p. 172°C (decomp.); *endo*-**4** (0.6 g 30%), m.p. 161°C (decomp.). − *exo*-**4**: ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.28 (t, J = 1.8 Hz, 2 H, 7-H, 8-H), 4.52 (m, 2 H, 1-H, 4-H), 6.65 (dd, J = 4.1 Hz, J = 3.1 Hz, 2 H, 5-H, 6-H), 7.16 (dd, J = 5.4 Hz, J = 3.4 Hz, 2 H, 10-H, 11-H), 7.28 (dd, 2 H, 9-H, 12-H). − ^{13}C NMR (75 MHz, CDCl$_3$, DEPT, C,H COSY): δ = 41.76 (CH, C-1, C-4), 47.38 (CH, C-7, C-8), 123.91 (CH, C-9, C-12), 126.63 (CH, C-10, C-11), 134.88 (CH, C-5, C-6), 140.83 (C, C-2, C-3), 170.93 (C, C=O). − FT IR (KBr): ṽ = 3043, 3017 cm^{-1} (C−H), 2979, 2959 (C−H), 1774 (C=O), 1465, 1458 (C=C), 1221, 1078 (C−O), 926, 766, 735 (C−H). − MS (70 eV); *m/z* (%): 226 (12) [M$^+$], 181 (3), 153 (10), 128 (100) [C$_{10}$H$_8$$^+$], 102 (3), 76 (9) [C$_6H_4$$^+$], 51 (4) [C$_4H_3$$^+$]. − C$_{14}H_{10}O_3$: calcd. 226.0630, found 226.0622 (MS). − *endo*-**4**: ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.42 (dd, J = 2.3 Hz, J = 1.5 Hz, 2 H, 7-H, 8-H), 4.46 (m, 2 H, 1-H, 4-H), 6.69 (dd, J = 4.3 Hz, J = 3.0 Hz, 2 H, 5-H, 6-H), 7.17 (m, 2 H, 10-H, 11-H), 7.22 (m, 2 H, 9-H, 12-H). − ^{13}C NMR (75 MHz, CDCl$_3$, DEPT, C,H COSY): δ = 41.78 (CH, C-1, C-4), 47.68 (CH, C-7, C-8), 124.73 (CH, C-9, C-12), 127.21 (CH, C-10, C-11), 135.99 (CH, C-5, C-6), 138.35 (C, C-2, C-3), 170.36 (C, C=O). − FT IR (KBr): ṽ = 3041, 3009 cm^{-1} (C−H), 2977, 2955 (C−H), 1792 (C=O), 1472, 1461 (C=C), 1223, 1081 (C−O), 927, 758, 730 (C−H). − MS (70 eV); *m/z* (%): 226 (6) [M$^+$], 181 (3), 153 (8), 128 (100) [C$_{10}$H$_8$$^+$], 102 (3), 76 (4) [C$_6H_4$$^+$], 51 (3) [C$_4H_3$$^+$]. − C$_{14}H_{10}O_3$: calcd. 226.0630; found 226.0621 (MS).

Pressure Dependence of the Ratio of [6]/[*exo*-4]/[*endo*-4] in the Diels−Alder Reaction of 6 with 7: Portions of 0.8 mL of a mixture containing **6** (50 mg, 0.39 mmol), freshly sublimed **7** (38 mg, 0.39 mmol), 8 mg of acetonitrile as internal standard and 8 mL of anhydrous CDCl$_3$ were sealed in PTFE tubes and heated at different pressures at 100°C for 22 h as stated in Table 1. The ratio of **6**/ *exo*-**4**/*endo*-**4** were analyzed by ^{1}H NMR (300 MHz) using the integration of the signals at δ = 7.7 (**6**), 3.28 (*exo*-**4**), 3.42 (*endo*-**4**). − *endo*- and *exo*-**8** were prepared by Diels−Alder reaction of 6,6-dimethylfulvene (**10**) with *N*-phenylmaleic imide (**11**) according to the corresponding reactions of **10** with maleic anhydride.[18]

***endo*-7-Isopropylidene-*N*-phenylbicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic Imide (*endo*-8):**[19] **10** (1.00 g, 9.42 mmol) was added to a stirred solution of **11** (1.63 g, 9.43 mmol) in 20 mL of diethyl ether. The mixture was stirred for 24 h at room temperature. The precipitated colorless solid consisting of *endo*-**8** was filtered, washed with a small quantity of diethyl ether and dried with air. Yield 1.94 g (74%), m.p. 150°C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.58 (s, 6 H, 9-H, 10-H), 3.35 (dd, J = 2.9 Hz, J = 1.5 Hz, 2 H, 5-H, 6-H), 3.91 (m, 2 H, 1-H, 4-H), 6.37 (t, J = 2.0 Hz, 2 H, 2-H, 3-H), 7.12, 7.37 (2 m, 5 H, H$_{arom}$).

***exo*-7-Isopropylidene-*N*-phenylbicyclo[2.2.1]hept-2-ene-5,6-dicarboxylic Imide (*exo*-8):** **10** (4.30 g, 40.6 mmol) was added to a stirred solution of **11** (6.93 g, 40.1 mmol) in 50 mL of toluene. The mixture was heated for 20 h at reflux. After cooling to room temperature, *exo*-**8** precipitated as colorless solid which was filtered and recrystallized from cyclohexane/ethyl acetate, 6:1. Yield: 6.70 g (60%). m.p. 158°C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.58 (s, 6 H, 9-H, 10-H), 2.88 (s, 2 H, 5-H, 6-H), 3.82 (t, J = 2.0 Hz, 2 H, 1-H, 4-H), 6.44 (t, 2 H, 2-H, 3-H), 7.09, 7.41 (2 m, 5 H, H$_{arom}$). − ^{13}C NMR (75 MHz, CDCl$_3$, DEPT, C−H-COSY): δ = 19.74 (2 CH$_3$, C-9, C-10), 46.14 (2 CH, C-1, C-4), 47.91 (2 CH, C-5, C-6), 115.56 (C, C-8), 126.31, 128.60, 129.18 (5 CH, C$_{arom}$), 131.89 (C, C$_{arom}$), 137.66 (2 CH, C-2, C-3), 140.62 (C, C-7), 176.58 (2 C, C=O). − FT IR (KBr): ṽ = 3062, 3012 cm^{-1} (C−H), 2981, 2914, 2855 (C−H), 1698 (C=O), 1592, 1493, 1453 (C=C), 1180 (C−N). − MS (70 eV), *m/z* (%): 279 (8) [M$^+$], 173 (37) [NPMI$^+$], 129 (11), 117 (14), 106 (100) [C$_8$H$_{10}$$^+$], 91 (52) [C$_7H_7$$^+$], 77 (11) [C$_6H_5$$^+$], 65 (9) [C$_5H_5$$^+$], 39 (12) [C$_3H_3$$^+$]. − C$_{18}H_{17}NO_2$: calcd. 279.1259; found 279.1260 (MS). − From the melting point (m.p. 161°C) reported for *endo*-**8**[19] it can be concluded that the Diels−Alder adduct isolated after recrystallization consists of *exo*-**8** instead of *endo*-**8**. The assignment of *endo*-**8** and *exo*-**8** unambiguously results from the coupling constant $^3J_{1,6}$ = $^3J_{4,5}$ = 2.9 Hz in the ^{1}H-NMR spectrum of *endo*-**8** which is missing in the spectrum of *exo*-**8**.

Pressure-Dependent Kinetic Measurements of Retro Diels−Alder Reactions

General: A solution of the corresponding Diels−Alder adducts in an organic solvent (8−10 mL) was thermolyzed as described above. For each pressure, five to nine samples were released and analyzed by GC and HPLC, respectively. From the time dependence of the disappearance of starting material versus the internal standard (in case of the HPLC anaysis of *endo*-**4** and *exo*-**4** the constant volume of the injected sample was used as internal standard) the specific rate constants k (Table 2) were calculated by using the kinetic law for first-order irreversible reactions.

Thermolysis of 1a: Portions of a solution of **1a** (640 mg) and *n*-nonane (622 mg) as internal standard in 250 mL of *n*-hexane were thermolyzed at 105.3°C and seven different pressures (Table 2). The samples were analyzed by GC [column A; injector: 160°C; column: programmed temperature 40°C/5 min; 10°C/min; 120°C/2 min; t_{R}(**3a**) = 4.8 min; t_{R}(*n*-nonane) = 8.4 min; t_{R}(**1a**) = 10.0 min].

Thermolysis of 1b: Portions of a solution of **1b** (1.156 g) and *n*-tridecane (1.158 g) as internal standard in 130 mL of toluene were thermolyzed at 105.6°C at eight different pressures (Table 2). The samples were analyzed by GC [column B; injector: 153°C; column: 115°C (isothermal); t_{R}(**3b**) = 5.7 min; t_{R}(*n*-tridecane) = 6.3 min; t_{R}(**1b**) = 18.1 min].

Thermolysis of *endo*-4: Portions of a solution of *endo*-**4** (1.41 g) in 200 mL of *tert*-butyl methyl ether (MTBE)/acetonitrile (90:10) were thermolyzed at 106.3°C at 16 different pressures between 200 and 4000 bar (Table 2). Samples were analyzed by HPLC [column D; mobile phase MTBE/heptane, 80:20; flow 0.6 mL/min; detection: UV (254 nm); t_{R}(**6**) = 2.2 min; t_{R}(**7**) = 2.6 min; t_{R}(*endo*-**4**) = 3.5 min].

Thermolysis of *exo*-4: Portions of a solution of *exo*-**4** (1.30 g) in 120 mL of MTBE/acetonitrile (90:10) were thermolyzed at 106.3°C at 11 different pressures between 200 and 4000 bar (Table 2). Samples were analyzed by HPLC [column C; mobile phase MTBE/heptane, 50:50; flow 0.4 mL/min; detection: UV (254 nm); t_{R}(**6**) = 6.4 min; t_{R}(*exo*-**4**) = 7.6 min; t_{R}(**7**) = 11.5 min].

Thermolysis of *endo*-8: Portions of a solution of *endo*-**8** (166 mg) and naphthalene **6** (165 mg) as internal standard in 200 mL of methanol were thermolyzed at 87.0°C at 11 different pressures between 200 and 3500 bar (Table 2). Samples were analyzed by HPLC [column E; mobile phase methanol/water, 70:30; flow 0.7 mL/min; detection: UV (230 nm); t_{R}(**11**) = 1.9 min; t_{R}(*endo*-**8**) = 2.9 min; t_{R}(**10**) = 4.1 min; t_{R}(**6**) = 5.1 min].

Thermolysis of *exo*-8: Portions of a solution of *exo*-**8** (135 mg) and naphthalene (134 mg) as internal standard in 160 mL methanol were thermolyzed at 121.7°C at 12 different pressures between 200 and 4000 bar (Table 2). The samples were analyzed by HPLC [column E; mobile phase methanol/water, 70:30; flow 0.7 mL/min; detection: UV (230 nm); t_{R}(**11**) = 2.0 min; t_{R}(*endo*-**8**) = 2.8 min; t_{R}(**10**) = 4.1 min; t_{R}(**6**) = 5.1 min].

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