

described before to give 160 mg of crude 19, which was purified by MPLC (RP 18, CH<sub>3</sub>OH/H<sub>2</sub>O = 9:1). Yield: 119 mg (82%) of 19 and traces (20 mg) of a bisadduct, which has not been purified.

**6-Methylene-3-phenyl-1,2-oxazaspiro[4.4]non-2-ene (19):** mp 42–43 °C (pentane); IR (neat) 2946, 1444, 1357, 915, 757, 690 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.63–2.72 (m, 8 H), AB system with  $\nu_A = 3.27$ ,  $\nu_B = 3.44$ , and  $J_{AB} = 17.0$  Hz (2 H), 5.13 (mc, 1 H), 5.21 (mc, 1 H), 7.37–7.42 (m, 3 H), 7.66–7.71 (m, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 22.12 (t), 31.10 (t), 40.01 (t), 45.14 (t), 92.78 (s), 108.50 (t), 126.52 (d), 128.66 (d), 129.86 (d), 129.98 (s), 153.43 (s), 155.91 (s); mass spectrum (70 eV), *m/z* (relative intensity) 213 (M<sup>+</sup>, 36), 212 (18), 196 (8), 185 (6), 184 (8), 117 (100), 104 (9), 103 (7), 95 (9), 94 (21), 93 (8), 91 (11), 79 (34), 77 (34); high resolution mass spectrum, *m/z* calcd for C<sub>14</sub>H<sub>15</sub>NO 213.11536, found 213, 11519. Anal. Calcd for C<sub>14</sub>H<sub>15</sub>NO (213.3): C, 78.84; H, 7.09; N, 6.57. Found: C, 78.84; H, 6.95; N, 6.35.

**Solvent Dependence of the Product Ratio from 1a and 5.** The reaction was carried out with equimolar amounts of 1a and 5 at ambient temperature in different solvents as described for ether (see above).<sup>19</sup> The crude product mixture was analyzed by <sup>1</sup>H NMR using the singlets at δ 5.04 and 5.07 for 8, the singlets at δ 5.58 and 6.43 for 9, and the singlet at δ 6.09 for 10. The small

amounts of 11 have been neglected.

solvent	8:9:10	8:(9+10)
hexane	8:1:1	4.0
CCl <sub>4</sub>	5.8:1.7:1	2.1
Et <sub>2</sub> O	10.1:2.7:1	2.7
CH <sub>2</sub> CN	6.0:1.8:1	2.1

**Relative Reactivities of Dipolarophiles toward Benzonitrile Oxide (1a).** A mixture of two dipolarophiles and benzo-hydroxamoyl chloride were dissolved in 4 mL of CCl<sub>4</sub>. Triethylamine was added, and the mixture was stirred at 20.5 °C for 8 h. The mixture was filtered to remove triethylammonium hydrochloride, and the filtrate was concentrated under reduced pressure to give a mixture of products, which was analyzed by <sup>1</sup>H NMR or GC.

The <sup>1</sup>H NMR analyses were based on the relative intensities of the following signals: 8, δ 5.04 and 5.07 (2 s, 2 H); 16, δ 5.70, (dd, 1 H); 17, δ 5.51, (s, 1 H).

The GC separation was carried out on a 50-m SE 30 fused-silica capillary column (id 0.2 mm) at 270 °C. Compounds 8, 16, and 19 had retention times of 7.66, 5.87, and 4.72 min, respectively. For the evaluation of the product ratios, area factors of 0.5934 (8), 1.000 (16), and 0.6448 (19) were used.

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(19) The deviation of the 8:9:10 product ratio (ether) from that reported above is due to the use of 1a and 5 in a 1:1 ratio (2:1 in the previous experiment), which reduces the probability of the sequential reaction of 1a with 9 to give 10.

## Stepwise [4 + 2]- and [4 + 4]-Cyclodimerizations of 1,1,2,2,3,3-Hexamethyl-4,5-bis(methylene)cyclopentane

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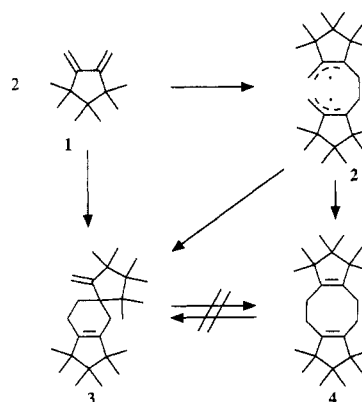
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The thermal dimerization of the title compound 1 yields the [4 + 2]-cyclodimer 3 and the [4 + 4]-cyclodimer 4 in a ratio of approximately 3.5:1. Comparison of activation enthalpies ( $\Delta H^\ddagger(3) = 80.1$  kJ/mol,  $\Delta H^\ddagger(4) = 76.6$  kJ/mol) and activation entropies ( $\Delta S^\ddagger(3) = -143.1$  J/mol K,  $\Delta S^\ddagger(4) = -163.3$  J/mol K) indicates both cycloadditions proceed by analogous mechanisms. A study of the pressure dependence (0.5–9.3 kbar) yields activation volumes in the same order of magnitude for both dimerizations ( $\Delta V_0^\ddagger = -(15$  to  $16)$  cm<sup>3</sup>/mol), indicative of two parallel stepwise processes. A selective cyclodimerization of 1 to give the [4 + 2]-cyclodimer 3 is achieved by acid catalysis.

Dimerizations of 1,3-dienes have attracted great attention in the mechanistic discussion of Diels–Alder reactions<sup>1</sup> since the regular [4 + 2]-cyclodimers are often accompanied by certain amounts of 1,2-divinylcyclobutanes and 1,5-cyclooctadienes.<sup>1–3</sup> The question of whether the diradical pathway, which accounts for the formation of the four- and eight-membered ring compounds, also represents the dominant route to the Diels–Alder products has been intensively studied, and evidence for concerted and stepwise Diels–Alder reactions has been presented.<sup>1</sup> Since in most cases the studies have been carried out with acyclic dienes, the analysis of the results is complicated by the conformational freedom of the dienes.

A conformationally rigid diene fragment with sterically shielded 2- and 3-positions is incorporated in the bis(methylene)cyclopentane 1.<sup>4</sup> Since this compound has

Scheme I



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been found to give a higher amount of 1,4-adducts than other dienes in several cycloadditions,<sup>5</sup> it appeared to be

Scheme II

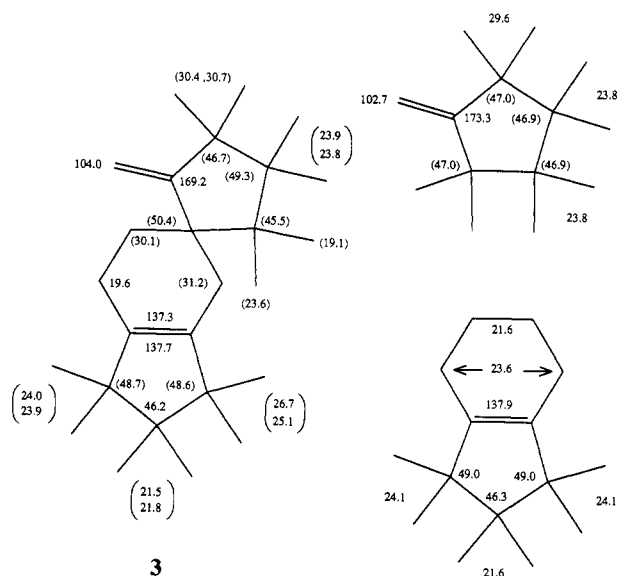


Table I. Activation Parameters for the Dimerization of 1 Derived from the Rate Constants Measured between 80 and 150 °C

reaction	$\Delta H^\ddagger$ , kJ mol <sup>-1</sup> (kcal mol <sup>-1</sup> )	$\Delta S^\ddagger$ , J mol <sup>-1</sup> K <sup>-1</sup> (cal mol <sup>-1</sup> K <sup>-1</sup> )
disappearance of 1	77.6 ± 0.9 (18.5 ± 0.2)	-144.6 ± 2.2 (-34.6 ± 0.5)
formation of 3	80.1 ± 1.5 (19.1 ± 0.4)	-143.1 ± 4.0 (-34.2 ± 1.0)
formation of 4	76.6 ± 1.5 (18.3 ± 0.4)	-163.3 ± 3.9 (-39.0 ± 0.9)

a suitable model compound for the mechanistic study of competing [4 + 2]- and [4 + 4]-cyclodimerizations.

**Thermal Dimerization of 1.** When a 50% solution of 1 in toluene was heated at 125 °C for 60 h, the [4 + 2]-cyclodimer 3 and the [4 + 4]-cyclodimer 4 were produced in 61 and 16% yield, respectively (Scheme I). The high symmetry of compound 4 is evident from its NMR spectra (six <sup>13</sup>C NMR signals), and the structural assignment of the Diels-Alder adduct 3 is based on the comparison of the <sup>13</sup>C NMR spectra of 3 and of model compounds (Scheme II).<sup>6</sup>

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Table II. Second-Order Kinetics for the Dimerization of 1 in Toluene

T, °C	$k_2(\text{total})$	$k_2(3)$	$k_2(4)$	$k_2(3)/k_2(4)$
80	$6.74 \times 10^{-7}$	$3.32 \times 10^{-7}$	$0.97 \times 10^{-7}$	3.4
100	$3.13 \times 10^{-6}$	$1.65 \times 10^{-6}$	$0.44 \times 10^{-6}$	3.7
125	$1.51 \times 10^{-5}$	$0.90 \times 10^{-5}$	$0.23 \times 10^{-5}$	3.9
150	$6.54 \times 10^{-5}$	$3.62 \times 10^{-5}$	$0.86 \times 10^{-5}$	4.2

When neat samples of 3 and 4 were heated at 150 °C for 9 h, a small degree of decomposition was observed, but no mutual interconversion of the two cycloadducts was detectable. Kinetic control of the 3/4 product ratio is also supported by the constancy of this ratio during the course of the kinetic experiments. As the product ratio is not affected by the presence of triethylamine during the dimerization, acid or base catalysis (see below) cannot account for the product ratio obtained under these conditions.

Since the [ $\pi 4_s + \pi 4_s$ ]-cycloaddition is an orbital symmetry forbidden process, the dimerization of 4 is rationalized by the intermediacy of the diradical 2. The Diels-Alder dimer 3 may also be generated via cyclization of 2, but for its formation a concerted pathway is also feasible. In order to distinguish between these two mechanistic possibilities, we have investigated the temperature- and pressure-dependence of the dimerization of 1.

The activation parameters presented in Table I were determined from the temperature dependence of the rate constants (Table II). The activation entropy for the formation of 3 is in the same order of magnitude as in other Diels-Alder reactions.<sup>16</sup> Its value ( $\Delta S^\ddagger(3)$ ) is less negative, however, than  $\Delta S^\ddagger(4)$ , which corresponds to a reaction where a diradical pathway is operative. Since concerted cycloadditions are characterized by more highly ordered transition states than the corresponding stepwise processes, the relative magnitude of  $\Delta S^\ddagger(3)$  and  $\Delta S^\ddagger(4)$  provides an argument that 3 is not formed by a concerted pathway while 4 is generated via the diradical 2. Further evidence for a stepwise Diels-Alder reaction comes from the observation that the activation enthalpy  $\Delta H^\ddagger(3)$  is higher by  $0.84 \pm 0.09$  kcal/mol than  $\Delta H^\ddagger(4)$ .<sup>7</sup> Steric effects which disfavor the concerted [4 + 2]-cycloaddition obviously overcompensate the gain of resonance energy (energy of concert)<sup>8</sup> resulting from a concerted bond formation in the Diels-Alder fashion.

This conclusion is corroborated by investigations at variable pressure. In the range from 1 to 9300 bar (80 °C) the product ratio 3:4 was found to be almost constant, indicating the activation volumes of the [4 + 2]- and the [4 + 4]-cycloaddition to be equal within the limits of 1 cm<sup>3</sup>/mol ( $\Delta V_0^\ddagger(3) - \Delta V_0^\ddagger(4) = -0.3$  cm<sup>3</sup>/mol, from Table III). This finding suggests a similar geometry of the transition states for the formation of both products. Again with the assumption that formation of 4 involves a stepwise process, 3 is accordingly the product of a nonconcerted Diels-Alder reaction.

The absolute values of the activation volumes for the formation of 3 and 4 were determined from the pressure dependence of the corresponding rate constants  $k_2(3)$  and  $k_2(4)$  at 79.1 °C between 550 and 9300 bar (Table III) to be  $\Delta V_0^\ddagger(3) = -15.8 \pm 0.2$  cm<sup>3</sup>/mol and  $\Delta V_0^\ddagger(4) = -15.5$

(6) (a) 1,1,2,2,3,3,4,4-Octamethyl-5-methylenecyclopentane: Wehle, D.; Scheuermann, H. J.; Fitjer, L. *Chem. Ber.* 1986, 119, 3127-3140. (b) 7,7,8,8,9,9-Hexamethylbicyclo[4.3.0]non-1(6)-ene: Pock, R.; Mayr, H., unpublished results.

(7)  $\Delta\Delta S^\ddagger$  and  $\Delta\Delta H^\ddagger$  result from the temperature dependence of the product ratio [3]:[4] measured by GC very precisely.

(8) Doering, W. v. E.; Roth, W. R.; Breuckmann, R.; Figge, L.; Lenartz, H.-W.; Fessner, W.-D.; Prinzbach, H. *Chem. Ber.* 1988, 121, 1-9.

**Table III. Pressure Dependence of the Dimerization of 1 at 79.1 °C**(a)  $[1]_0 = 0.246$  M;  $[n\text{-C}_{18}\text{H}_{38}] = 0.107$  M;  $[\text{BHMPs}] = 0.061$  M in toluene(b)  $[1]_0 = 0.258$  M;  $[n\text{-C}_{18}\text{H}_{38}] = 0.091$  M;  $[\text{Ph}_2\text{NH}] = 0.140$  M in toluene

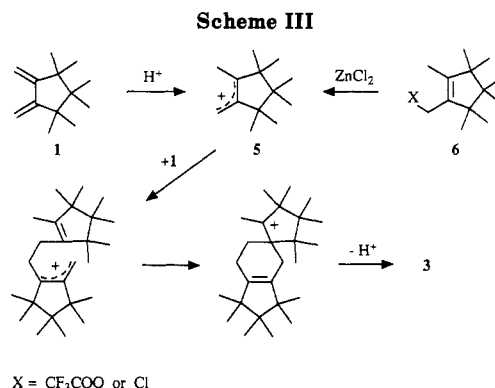
	pressure, bar	time, h	convn of 1, %	[3]/[4]	recovery, %	$k_2(3)^a$	$k_2(4)^a$
(a)	550	66	5.5	3.07	99.1	0.616	0.203
	1350	67	7.2	3.09	100.0	0.994	0.322
	2250	45	9.8	3.14	98.2	1.69	0.539
	2600	21	4.5	3.18	99.5	1.71	0.539
	3800	21	9.1	3.23	97.1	2.84	0.881
	5500	16	11.6	3.43	97.2	5.40	1.58
	5800	21	15.1	3.46	97.6	6.23	1.80
	9300	21	23.0	4.02	95.6	16.3	4.06
(b)	550	66	5.2	3.04	99.6	0.625	0.206
	1350	67	9.9	3.11	97.4	0.989	0.317
	2250	45	8.2	3.17	99.9	1.58	0.497
	2600	21	4.4	3.13	100.0	1.78	0.567
	3800	21	8.1	3.27	98.8	2.96	0.906
	5500	16	13.9	3.46	95.6	5.71	1.65
	5800	21	13.8	3.43	99.0	5.89	1.72
	9300	21	30.4	4.02	97.9	16.7	4.14
		$\Delta V^*(3)^b$	$\Delta V_0^*(3)^b$	$\Delta V^*(4)^b$	$\Delta V_0^*(4)^b$		
(a)		$-15.3 \pm 1.6$	$-15.8 \pm 0.2$	$-14.7 \pm 1.7$	$-15.5 \pm 0.2$		
(b)		$-15.1 \pm 0.7$	$-15.9 \pm 0.1$	$-14.6 \pm 0.5$	$-15.5 \pm 0.1$		

<sup>a</sup>  $\times 10^6$  [L mol<sup>-1</sup> s<sup>-1</sup>]. <sup>b</sup> [cm<sup>3</sup>/mol].

$\pm 0.2$  cm<sup>3</sup>/mol, respectively. From the partial molar volumes of 1 and 3 the reaction volume for the formation of 3 was derived to be  $\Delta V(3) = -40.8$  cm<sup>3</sup>/mol at 21 °C and  $-51.2$  cm<sup>3</sup>/mol at 79.1 °C (extrapolated by using the Eyring equation<sup>9</sup>). The activation volume  $\Delta V_0^*(3)$  is considerably less negative than that of most common Diels-Alder reactions ( $\Delta V^* = -25$  to  $-40$  cm<sup>3</sup>/mol<sup>16,10</sup> whereas the corresponding reaction volume is in the usual order of magnitude. The ratio  $\Delta V_0^*(3)/\Delta V(3) = 0.31$  indicates that contrary to concerted Diels-Alder reactions (where the ratio  $\Delta V_0^*/\Delta V$  is usually found to be equal to or even larger than unity) the geometry of the transition state of this reaction does not resemble that of the product. Consequently, the [4 + 2]-cycloaddition like the [4 + 4]-cycloaddition of 1 proceeds through the intermediary of a diradical.

**Catalyzed Dimerization of 1.** Attempts to synthesize 4 selectively via Ni-catalyzed dimerization<sup>11</sup> of 1 have failed. No reaction took place when 1 was heated with Ni(COD)<sub>2</sub>/Ph<sub>3</sub>P<sup>12</sup> at 60 °C in toluene for 18 h. A selective [4 + 2]-dimerization was observed, however, when 1 was treated with ZnCl<sub>2</sub>/Et<sub>2</sub>O in dichloromethane<sup>13</sup> at ambient temperature. Proton catalysis from traces of moisture, as indicated in Scheme III, is probably responsible for this dimerization process, since ZnCl<sub>2</sub>·OEt<sub>2</sub> was inefficient in the presence of 0.2 equiv of NEt<sub>3</sub>. In accord with this interpretation, the Brønsted basic Lewis acid Et<sub>2</sub>AlCl did not induce a reaction, while BF<sub>3</sub>·OEt<sub>2</sub> gave rise to the formation of 3 and of polymers even at  $-70$  °C.

Moderately strong Brønsted acids per se are, however, not sufficient for the dimerization of 1, since a 1:1 mixture of 1 and 6 (X = CF<sub>3</sub>CO<sub>2</sub>)<sup>14</sup> was observed when 0.5 equiv



of CF<sub>3</sub>CO<sub>2</sub>H was added to a CCl<sub>4</sub> solution of 1 at ambient temperature. Similarly, mixtures of 1 and 6 (X = Cl)<sup>15</sup> were obtained when hydrogen chloride (<1 equiv) was introduced into solutions of 1 in CH<sub>2</sub>Cl<sub>2</sub> at  $-70$  °C or at ambient temperature. The formation of 3 was observed, however, when 1% of trifluoromethanesulfonic acid was added to a solution of 1 in dichloromethane at  $-70$  °C and warmed up to room temperature. Further support for the mechanism presented in Scheme III comes from the following experiment: When 6 (X = Cl, 0.1 mmol) was added to a solution of 1 (0.4 mmol), ZnCl<sub>2</sub> (2.0 mmol)/Et<sub>2</sub>O (3.2 mmol), and NEt<sub>3</sub> (0.4 mmol), 6 consumed 1 equiv of 1 to give 3, while the rest of the diene remained unaffected.

## Experimental Section

**General.** The NMR spectra were taken on a Varian XL 200 spectrometer with tetramethylsilane as internal standard. The mass spectra were recorded on a 70-250 VG spectrometer, and the microanalyses were carried out by Ilse Beetz, Microanalytisches Laboratorium, D-8640 Kronach.

**Thermal Dimerization of 1.** Compound 1 (0.67 g) and toluene (0.60 g) were heated for 60 h at 125 °C in a stoppered flask, which had been flushed with nitrogen. The product mixture was separated by MPLC (RP18, methanol) to give 0.35 g (52%) of 3 and

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(13) Mayr, H.; Striepe, W. *J. Org. Chem.* 1985, 50, 2995-2998.

(14) <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  0.81 (s, 6 H), 0.92 (br s, 12 H), 1.67 (s, 3 H), 4.88 (s, 2 H).

(15) <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  0.80 (s, 6 H), 0.92 (s, 6 H), 1.00 (s, 6 H), 1.43 (s, 3 H), 3.98 (s, 2 H).

Table IV

compound	area factor	retention time, min
CH <sub>2</sub> Cl <sub>2</sub>		4.25
mesitylene		4.38
1	1.046	4.59
PhC <sub>12</sub> H <sub>25</sub>	1.000	6.05
3	1.1117	11.54
4	1.1117	12.27

0.09 g (13%) of 4 with 0.10 g (15%) of unreacted diene 1.

**7,7,8,8,9,9,2',2',3',3',4',4'-Dodecamethyl-5'-methylene-*spiro*[bicyclo[4.3.0]non-1(6)-ene-3,1'-cyclopentane] (3):** mp 110–111 °C (from ethanol); IR (KBr) 2973, 2942, 2867, 2824, 1637, 1475, 1456, 1441, 1428, 1399, 1382, 1372, 1365, 1144, 1124, 888, 677 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.80 (br, s, 9 H), 0.84 (s, 3 H), 0.86 (br s, 9 H), 0.89 (s, 3 H), 0.91 (s, 3 H), 1.05 (s, 6 H), 1.09 (s, 3 H), 1.45–1.67 (m, 2 H), 1.80–2.02 (m, 4 H), 4.84 (br s, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) see Scheme II; mass spectrum (70 eV) *m/z* (relative intensity) 356 (M<sup>+</sup>, 7), 341 (30), 229 (100), 215 (23), 163 (29), 149 (21), 57 (62). Anal. Calcd for C<sub>26</sub>H<sub>44</sub> (356.6): C, 87.56; H, 12.44. Found: C, 87.78; H, 12.39.

**5,5,6,6,7,7,12,12,13,13,14,14-Dodecamethyltricyclo[9.3.0.0<sup>4,8</sup>]tetradeca-1(11),4(8)-diene (4):** mp 105–105.5 °C (from methanol); IR (KBr) 2975, 2940, 2907, 2870, 2827, 1474, 1461, 1438, 1391, 1374, 1364, 1150, 1111, 1094, 1048 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.75 (s, 12 H), 0.86 (s, 24 H), 2.31 (s, 8 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 21.66 (q), 24.80 (q, double int), 25.01 (t), 45.66 (s), 50.42 (s, double int) 138.38 (s); mass spectrum (70 eV), *m/z* (relative intensity) 356 (M<sup>+</sup>, 30), 341 (100), 229 (19), 191 (24), 163 (71), 149 (56), 57 (56). Anal. Calcd for C<sub>26</sub>H<sub>44</sub> (356.6): C, 87.56; H, 12.44. Found: C, 87.58; H, 12.35.

**Temperature Dependence of the Dimerization of 1.** A solution of 1 (1.204 g) and dodecylbenzene (0.647 g, internal standard) was dissolved in mesitylene to give a total of 5.00 mL. Portions (0.2 mL) were placed in vials with Teflon-coated screw caps, flushed with nitrogen, and placed in a thermostat. After the vials had been removed from the thermostat, 1 mL of CH<sub>2</sub>Cl<sub>2</sub> was added, and the solutions thus obtained were analyzed by GC (Shimadzu GC 9A, fused silica (SE30) capillary column, i.d. 0.20 mm, length 50 m, 270 °C column temperature, N<sub>2</sub> carrier gas).

The rate constants *k*<sub>2</sub>(total) were obtained from the slopes of 1/[1] versus *t* plots, which were linear up to 80–90% conversion. Quantitative analysis of the products 3 and 4 allowed splitting of *k*<sub>2</sub>(total) into the partial rate constants *k*<sub>2</sub>(3) and *k*<sub>2</sub>(4). With increasing time, the sum of [1], [3], and [4] is decreasing, indicating the formation of a nonvolatile unknown side product (probably polymer). Consequently, the sum of *k*<sub>2</sub>(3) and *k*<sub>2</sub>(4) is somewhat smaller than *k*<sub>2</sub>(total).

**Pressure Dependence of the Dimerization of 1.** Portions (0.2 mL) of the solution of 1, *n*-C<sub>18</sub>H<sub>38</sub> (as internal GC standard), and (a) bis(3-*tert*-butyl-4-hydroxy-5-methylphenyl) sulfide (BHMPs) or (b) diphenylamine (Ph<sub>2</sub>NH) (as inhibitors of radical chain polymerization of 1) in toluene (degassed and saturated with argon) were sealed in PTFE tubes (pretreated with refluxing triethylamine in order to avoid acid catalysis at the surface of the PTFE tubes), placed in a 10-kbar autoclave, and heated at different pressures as stated in Table III. The degree of conversion and the product ratio [3]:[4] were analyzed by GC, using a Sichromat 2 (Siemens). Column: silicon oil OV 1 25 m fused silica. Temperature program: 170 °C (8 min) → 295 °C (11–16 min). Rate of heating: 25 °C/min. Carrier gas: helium. Retention time [min]: 7.2 (1), 12.7 (Ph<sub>2</sub>NH), 15.8 (*n*-C<sub>18</sub>H<sub>38</sub>), 22.9 (3), 23.5 (4), 27.5 (BHMPs). The pressure-dependent rate constants *k*<sub>2</sub>(3) and *k*<sub>2</sub>(4) shown in Table III were calculated from the disappearance of 1 and the formation of 3 and 4 according to the second-order rate law. The activation volume Δ*V*<sup>\*</sup> was calculated from the slope of the correlation ln *k*<sub>2</sub>(*p*) = *a*<sub>1</sub> + *b*<sub>1</sub>*p*, which holds up to a pressure of *p* = 2600 bar (Δ*V*<sup>\*</sup> = -*b*<sub>1</sub>*RT*). Δ*V*<sub>0</sub><sup>\*</sup> was derived from the nonlinear correlation ln *k*<sub>2</sub>(*p*) = *a*<sub>2</sub> + *b*<sub>2</sub>*p* + *c*<sub>2</sub>*p*<sup>2</sup>, which is valid in the whole pressure range investigated (Δ*V*<sub>0</sub><sup>\*</sup> = -*b*<sub>2</sub>*RT*).<sup>16</sup>

**Reaction Volume of the Cyclodimerization of 1 to 3.** The partial molar volumes of 1 and 3 were determined from the density of solutions measured for various concentrations of 1 and 3 in toluene at 21 °C: *V* [cm<sup>3</sup>/mol] of 1 201.9 ± 0.5; 3 363.0 ± 0.3. The molar volumes were additionally calculated using group increments (with corrections for the nearest neighbors) published by O. Exner.<sup>17</sup> The calculated values (*V*(1) = 201, *V*(3) = 362 cm<sup>3</sup>/mol) are in good agreement with the values determined from the densities. The reaction volume of the cyclodimerization is calculated to be Δ*V* = 363.0 - (2 × 201.9) = -40.8 cm<sup>3</sup>/mol. For a comparison with the activation volume, the reaction volume determined at 21 °C is extrapolated to 79.1 °C using the El'yanov equation:<sup>9</sup> Δ*V*(*T*<sub>1</sub>) = Δ*V*(*T*<sub>0</sub>)[1 + 0.0044(*T*<sub>1</sub> - *T*<sub>0</sub>)] = -51.2 cm<sup>3</sup>/mol.

**ZnCl<sub>2</sub>-Catalyzed Dimerization of 1.** Compound 1 (0.50 g, 2.8 mmol) was added to a stirred solution of ZnCl<sub>2</sub> (0.19 g)/Et<sub>2</sub>O (0.17 g) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub><sup>13</sup> at -70 °C. The cooling bath was removed, and stirring was continued for 3 h. The solution was washed with 10 mL of saturated aqueous Na<sub>2</sub>CO<sub>3</sub> solution and dried over MgSO<sub>4</sub>. After filtration and evaporation of the solvent, Kugelrohr distillation afforded 0.31 g (62%) of 3 with bp 210 °C (bath)/0.3 mbar.

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(17) Exner, O. *Empirical Calculations of Molar Volumes in Organic High Pressure Chemistry*; le Noble, W. J., Ed.; Elsevier: Amsterdam, 1988; pp 19–49.