159. Tandem Cheletropic Additions of Sulfur Dioxide to [2.2.2]Hericene. The 'Barrelene Effect'

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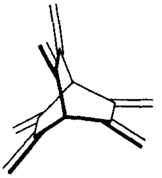
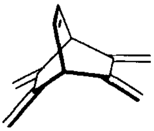
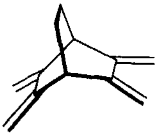
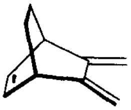
At 20°, [2.2.2]hericene (= 2,3,5,6,7,8-hexamethylidenebicyclo[2.2.2]octane; **1**) adds 2 equiv. of SO_2 to give successively mono-sulfolene **13** and the bis-sulfolene **14** (for thermodynamic and kinetic data, see *Tables 1* and *2*). Under forcing conditions (high concentration, long reaction time), no trace of tris-sulfolene **15** could be detected. The inertia of bis-sulfolene **14** is attributed to the 'barrelene effect' which destabilizes the tris-sulfolene **15**.

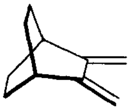
Introduction. – Strong dienophiles such as ethylenetetracarbonitrile (TCNE) add to [2.2.2]hericene (**1**) and the related exocyclic polyenes **2**–**5** with similar rate constants [1]. These results were consistent with predictions based on the PMO theory [2] since **1**–**5** have practically the same ionization energies in the gas phase [3–5]. X-Ray data on **1** [6] and related dienes grafted onto bicyclo[2.2.2]octane skeletons [7] as well as circular dichroism studies on derivatives of tetraene **3** [8] confirmed that these systems have planar s-*cis*-butadiene moieties with very similar geometries [1].











	1	**2**	**3**	**4**	**5**
IE [eV]:	8.38 [5]	8.37 [4]	8.36 [4]	8.33 [3]	8.37 [3]
$k^{II} \cdot 10^3$ [$dm^3 \cdot mol^{-1} \cdot s^{-1}$] (TCNE) at 298 K:	136	172	591	670	1900

Although the UV absorption [9–11] and photoelectron (PE) spectra [3] [5] confirmed the existence of significant transannular interactions [12] between the homoconjugated s-*cis*-butadiene moieties in **1**–**3**, their *Diels-Alder* reactivity was not affected by it as **1**–**3** added to TCNE with about the same rates as the parent diene **5** or triene **4**. Moreover, a hypothetical bishomoaromaticity between an endocyclic double bond and an exocyclic s-*cis*-butadiene moiety, as in **4** and **2**, appears to be insignificant by comparing kinetic and PE data of the polyene pairs **4**/**5** and **2**/**3**. In the light of these results, the three successive cycloadditions of TCNE to the triple diene **1** giving the corresponding mono-adduct **6** (k_1^{II}), bis-adduct **7** (k_2^{II}), and tris-adduct **8** (k_3^{II}) were expected to have rate

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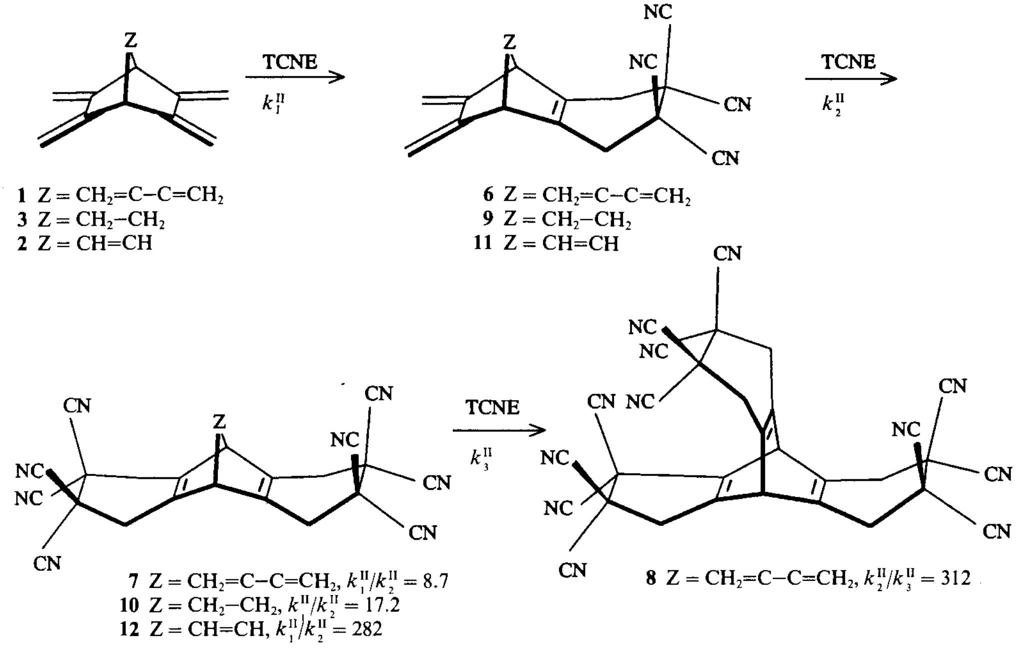


1 $Z = CH_2{=}C{-}C{=}CH_2$
3 $Z = CH_2{-}CH_2$
2 $Z = CH{=}CH$

6 $Z = CH_2{=}C{-}C{=}CH_2$
9 $Z = CH_2{-}CH_2$
11 $Z = CH{=}CH$

7 $Z = CH_2{=}C{-}C{=}CH_2$, $k_1^{II}/k_2^{II} = 8.7$
10 $Z = CH_2{-}CH_2$, $k^{II}/k_2^{II} = 17.2$
12 $Z = CH{=}CH$, $k_1^{II}/k_2^{II} = 282$

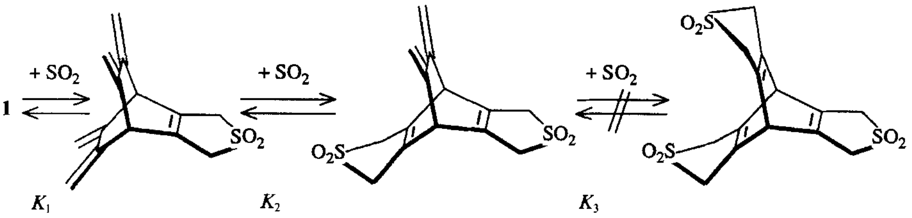
8 $Z = CH_2{=}C{-}C{=}CH_2$, $k_2^{II}/k_3^{II} = 312$

constants of the same order of magnitude. This is indeed the case for the first two reactions as one finds $k_1^{II}/k_2^{II} = 8.7$ at 25° (statistically corrected: $k_1^c/k_2^c = 5.8$). Unexpectedly, however, the cycloaddition of the third equiv. of TCNE occurs much more slowly as given by $k_2^{II}/k_3^{II} = 312$ at 25° (statistically corrected: $k_2^c/k_3^c = 156$). Noteworthy is the fact that cycloadditons **1** + TCNE→**6** and **6** + TCNE→**7** have, within experimental error limits, the same activation enthalpy ($\Delta H^{\neq} \approx 11$ kcal · mol^{-1}), whereas the addition **7** + TCNE→**8** has a significantly higher activation enthalpy ($\Delta H^{\neq} \approx 15$ kcal · mol^{-1}) [1].

Kinetic data [1] [13] showed that tetraene **3** can be considered to model the tandem *Diels-Alder* properties of [2.2.2]hericene (**1**), while pentaene **2** models those of the mono-adduct **6**. These results were interpreted in terms of variations in the exothermicity (ΔH_r) of the successive cycloadditions. In the cases of additions of TCNE to **1**–**5**, and of TCNE + **6**→**7** and TCNE + **9**→**10**, the exothermicities were all about the same, whereas in the case of reactions TCNE + **7**→**8** and TCNE + **11**→**12**, a smaller exothermicity was expected because the latter cycloadditions generated barrelene derivatives that are known to be destabilized by π-electron repulsion [14] arising from the specific arrangement of three endocyclic double bonds ('barrelene effect') [15]. Thus, because of the *Dimroth* [16] and *Bell-Evans-Polanyi* principle [17], the less exothermic reactions TCNE + **7**→**8** and TCNE + **11**→**12** are expected to be slower than the other, more exothermic reactions. An exothermicity difference of 6–10 kcal · mol^{-1} [14] may cause a change of 2–3 kcal · mol^{-1} in the $\Delta H^{\neq}$ term, as observed.

In contrast with the tandem *Diels-Alder* additions, the rate constants of the three successive photooxidations of **1** did not differ significantly [18]. This was consistent with the hypothesis that the photooxidations have near-zero activation enthalpies [19] and consequently should not be sensitive to a variation of the exothermicity of the reaction. In order to put the hypothesis of the 'barrelene effect' presented for the tandem *Diels-Alder* reactions of **1** and **2** on firmer ground, heats of the reactions considered should be measured. This has not been done yet, but, in the meantime, we have studied the tandem cheletropic additions of SO_2 to [2.2.2]hericene (**1**). These reactions present the advantage of being reversible near room temperature and, thus, allow one to evaluate both kinetic and thermodynamic parameters of the successive additions of SO_2. Our results are consistent with the existence of the 'barrelene effect' proposed to affect the tandem *Diels-Alder* reactivity of **1**.

Results. – On heating **1** in liquid SO_2 to 50° (sealed *Pyrex* tube), the bis-sulfolene **14**, contaminated by 2–3% of the mono-sulfolene **13**, was formed quantitatively. No trace of the corresponding tris-sulfolene **15** could be detected, even under forcing conditions such as: pure **14** + excess of SO_2 at −20, 0, 20, 40, or 50° for 3 months; or **1** + SO_2/CH_2Cl_2 1:1, 100°/20 atm for 2 days. The mono-sulfolene **13** was the major product (40%, isolated after column chromatography) by bubbling SO_2 through a solution of **1** in CH_2Cl_2 at −20, 0, 20, 40, or 50°.



13 **14** **15**

Attempts to catalyze the cheletropic additions of SO_2 with *Lewis* acids such as $BF_3 \cdot Et_2O$, $TiCl_4$, or $B(OAc)_3$ [20] led to the destruction of **1** at temperatures above −30°. The use of Me_3SiOTf and Et_3N [21] was not more successful. However, CF_3COOH induced a reaction of **1** with SO_2 that led to an unstable compound, probably a sultine intermediate [22], which rearranged at +20° (by 360-MHz ^1H-NMR) into the bis-sulfolene **14**. Under the latter conditions, no trace of tris-sulfolene **15** could be detected.

Equilibrium constants K_1 and K_2 (*Table 1*) of the two successive cheletropic additions of SO_2 to **1** were measured by 360-MHz ^1H-NMR at various temperatures and in two different solvents ($CDCl_3$, $(D_7)DMF$). *Van't Hoff* plots were established for 5–11 independent measurements for the temperature range 30–80°. They allowed one to evaluate the thermodynamical equilibrium parameters for $\mathbf{1} + SO_2 \rightleftarrows \mathbf{13}$ and $\mathbf{13} + SO_2 \rightleftarrows \mathbf{14}$ reported in *Table 1*.

In the absence of tris-sulfolene **15**, there is no way to evaluate equilibrium constant K_3 and the thermodynamical parameters associated with addition $\mathbf{14} + SO_2 \rightleftarrows \mathbf{15}$. Nevertheless, from the 360-MHz ^1H-NMR spectrum of bis-sulfolene **14** (showing no trace of **15**) equilibrated for 3 months at 30° with SO_2/DMF 3:1 (sealed NMR tube), with a signal/noise ratio > 200, a lower limit $K_3 < 4 \cdot 10^{-4}$ $dm^3 \cdot mol^{-1}$ was evaluated. It corresponds to $\Delta G_r(3) \geqslant 4.7$ $kcal \cdot mol^{-1}$ at 30°. Assuming $\Delta S_r(3) = \Delta S_r(2) = \Delta S_r(1) = -25$ $cal \cdot mol^{-1} \cdot K^{-1}$ for equilibria in $(D_7)DMF$ solutions, we estimate $\Delta H_r(3) \geqslant -3$ $kcal \cdot mol^{-1}$. Under similar conditions, no trace of **15** could be detected by 90.55-MHz ^{13}C-NMR.

The second-order rate constants k_1 and k_2 of the additions $\mathbf{1} + SO_2 \rightarrow \mathbf{13}$ and $\mathbf{13} + SO_2 \rightarrow \mathbf{14}$, respectively, were determined by 360-MHz ^1H-NMR and with the help of

Table 1. *Equilibrium Constants, Enthalpies, and Entropies of Reactions* **1** + SO_2⇄**13** (K_1) *and* **13** + SO_2⇄**14** (K_2)

	$CDCl_3$[a])		$(D_7)DMF$	
Temperature [°C]	30	80	30	80
K_1 [$dm^3 \cdot mol^{-1}$]	349 ± 83[b])	5.4 ± 1.3	21.3 ± 3	2.4 ± 1.3
K_2 [$dm^3 \cdot mol^{-1}$]	3.82 ± 0.3	0.35 ± 0.03	0.59 ± 0.08	0.11 ± 0.02
K_1/K_2	91.4	15.3	36.1	21.8
ΔG_1 [$kcal \cdot mol^{-1}$]	−3.5 ± 0.15	−1.16 ± 0.07	−1.84 ± 0.09	−0.6 ± 0.1
ΔG_2 [$kcal \cdot mol^{-1}$]	−0.81 ± 0.05	0.74 ± 0.06	0.32 ± 0.08	1.54 ± 0.1
$\Delta H_r(1)$ [$kcal \cdot mol^{-1}$]		−17.8 ± 2		−9.5 ± 1.2
$\Delta H_r(2)$ [$kcal \cdot mol^{-1}$]		−10.2 ± 0.7		−7.3 ± 1.2
$\Delta S_r(1)$ [$cal \cdot mol^{-1} \cdot K^{-1}$]		−47 ± 8		−25 ± 4
$\Delta S_r(2)$ [$cal \cdot mol^{-1} \cdot K^{-1}$]		−31 ± 2		−25 ± 4
Number of independent measurements	5	9	7(K_1), 8(K_2)	11(K_1), 6(K_2)
$\sigma(K_1)$	67	1.69	3.2	0.41
$\sigma(K_2)$	0.24	0.04	0.09	0.015

[a]) Corrections for the amount of SO_2 above the soln. were made.

[b]) Confidence range of 95%.

computer [23] non-linear least-square regressions of the kinetic data [24] for the two successive reactions under pseudo-first-order conditions (40- to 120-molar excess of SO_2; pseudo-first-order rate constants k_1' and k_2', with $k_1 = k_1'/[SO_2]$ and $k_2 = k_2'/[SO_2]$). The following second-order rate constants were obtained for reactions in $CDCl_3$ at +30°: $k_1 = (6.0 \pm 0.4) \cdot 10^{-5}$ $dm^3 \cdot mol^{-1} \cdot s^{-1}$, $k_2 = (1.76 \pm 0.05) \cdot 10^{-5}$ $dm^3 \cdot mol^{-1} \cdot s^{-1}$. In the case of the cheletropic additions in $(D_7)DMF$, the kinetic measurements were carried out at 30, 60, and 80° and allowed one to evaluate the activation parameters of the two successive reactions, using the *Arrhenius* relationship *(Table 2)*.

Discussion. – The thermodynamic parameters of equilibria **1** + SO_2⇄**13** and **13** + SO_2⇄**14** *(Table 1)* show a significant differential solvent effect on these reactions between apolar ($CDCl_3$) and dipolar solvent ((D_7)DMF). In the solvent of low dielectric constant ($CDCl_3$), the electric field associated with the dipole of a solute molecule penetrates the medium to larger distances than in a solvent of high dielectric constant ((D_7)DMF). Consequently, more molecules of solvent and SO_2 will contribute (be

Table 2. *Second-Order Rate Constants and Activation Parameters of the Successive Reactions* **1** + SO_2→**13** (k_1, $E_a(1)$, ln $A(1)$) *and* **13** + SO_2→**14** (k_2, $E_a(2)$, ln $A(2)$) *in* $(D_7)DMF$

Temperature [°C]	30	60	80
$k_1 \cdot 10^5$ [$dm^3 \cdot mol^{-1} \cdot s^{-1}$]	2.12	32.5	104.2
$k_2 \cdot 10^5$ [$dm^3 \cdot mol^{-1} \cdot s^{-1}$]	0.49	12.3	44.1
$k_1^c \cdot 10^5$[a])	0.71	10.8	34.7
$k_2^c \cdot 10^5$[a])	0.25	6.2	22.1
k_1^c/k_2^c	2.8	1.7	1.6
ln $A(1)$[b])	15.4 ± 2.0	ln $A(2)$[b])	18.2 ± 2.0
$E_a(1)$ [$kcal \cdot mol^{-1}$]	15.6 ± 1.3	$E_a(2)$	18.1 ± 1.3
$\Delta H^{\neq}(1)$ [$kcal \cdot mol^{-1}$]	15.0 ± 1.3	$\Delta H^{\neq}(2)$	17.5 ± 1.3
$\Delta S^{\neq}(1)$ [$cal \cdot mol^{-1} \cdot K^{-1}$]	−28.1 ± 4.0	$\Delta S^{\neq}(2)$	−22.6 ± 4.0

[a]) Second-order rate constants divided by the number of equivalent s-*cis*-butadiene moieties of the reacting polyene.

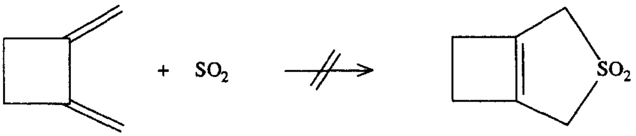
[b]) Derived from k_1 and k_2 values.

blocked by the dipole) to the solvation of the polar sulfolenes **13** and **14** in $CDCl_3$ than in $(D_7)DMF$. This is consistent with the observation of more negative entropies of reactions in $CDCl_3$ than in $(D_7)DMF$. Neither, in $CDCl_3$ nor in $(D_7)DMF$ **1** is expected to be strongly solvated. In $CDCl_3$ more likely than in $(D_7)DMF$, the number of solvent $+SO_2$ molecules blocked by the two sulfolene moieties of **14** will be less than twice that blocked in **13** since the two solvation spheres of the two sulfolene moieties of **14** overlap. This hypothesis is consistent with the observations $\Delta S_r(2) \approx \frac{2}{3}\, \Delta S_r(1)$ and $\Delta H_r(2) \approx \frac{2}{3}\, \Delta H_r(1)$ for the two successive SO_2 addition to **1** in $CDCl_3$, whereas $\Delta S_r(2) \approx \Delta S_r(1)$ and $\Delta H_r(2) \approx \Delta H_r(1)$ for the reactions in $(D_7)DMF$. It thus appears that only the data evaluated in the latter solvent can be considered for a comparison between the tandem cheletropic additions of SO_2 and the tandem *Diels-Alder* additions of [2.2.2]hericene (**1**).

16 $n = 4$
18 $n = 3$

17 $n = 4$
19 $n = 3$

Within experimental error limits, $\Delta H_r(1) = \Delta H_r(2)$ for the reactions in $(D_7)DMF$, and these values are only slightly higher than the heat of reaction ($\Delta H_r \approx -11.4$ kcal/mol) evaluated for equilibrium **16** + $SO_2 \rightleftarrows$ **17** and for the cheletropic additions of SO_2 to acyclic 1,3-dienes [25]. The SO_2 addition to 1,2-dimethylidenecyclopentane (**18**) is a slower reaction than that of 1,2-dimethylidenecyclohexane (**16**) [26]. Furthermore, the equilibrium constant of equilibrium **18** + $SO_2 \rightleftarrows$ **19** is *ca.* 625 times smaller than that of equilibrium **16** + $SO_2 \rightleftarrows$ **17** at 75° [26]. This difference was attributed to the strain increase when going from the bicyclic olefins **17** to **19**. Interestingly, 1,2-dimethylidenecyclobutane (**20**) does not react with SO_2, possibly on account of an even larger strain increase engendered when forming the bicyclo[3.2.0]hept-1(5)-ene system **21** [27].



20 **21**

In analogy with these results and interpretations, we propose that there is no significant strain increase when going from the sulfolene **13** to the bis-sulfolene **14** and that the nonobservation of tris-sulfolene **15** is associated with a significant strain increase when going from **14** to **15**. The latter is associated with the 'barrelene effect', an electronic destabilizing effect present in the barrelene derivatives **8** and **15**. In agreement with that hypothesis, all our attempts to add SO_2 to 7,8-dimethylidenebicyclo[2.2.2]octa-2,5-diene (**22**) [28] failed to yield the corresponding sulfolene **23**[2]).

Experiments have shown that cheletropic additions of SO_2 to 1,3-dienes are concerted suprafacial processes [31] comparable to *Diels-Alder* additions [32]. Isotopic effects con-

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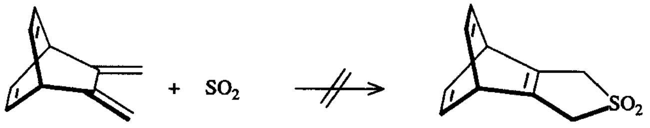
[2]) *Diels-Alder* additions to **22** were also found to be slower than those to related exocyclic s-*cis*-butadiene derivatives [28] [29] including **1**–**5** [30].



22 **23**

firmed early transition states for these reactions. This is also consistent with our observation that the rate-constant ratios $k_1/k_2 = 4.3$ (in (D_7)DMF) and 3.4 (in $CDCl_3$) are significantly smaller than the corresponding equilibrium-constant ratios $K_1/K_2 = 21.3$ (in (D_7)DMF) and 91.4 (in $CDCl_3$) at 30°. It is also consistent with the activation enthalpies $\Delta H^{\neq}(1)$ and $\Delta H^{\neq}(2)$ measured in (D_7)DMF which are found to be the same within limits of experimental errors, in parallel with the heat of reactions $\Delta H_r(1) \approx \Delta H_r(2)$.

Conclusion. – The reaction of [2.2.2]hericene (**1**) with SO_2 gives successively the sulfolene **13** and the bis-sulfolene **14**. In (D_7)DMF, the activation parameters of these two successive cheletropic additions are nearly the same as in the case of those of the successive *Diels-Alder* additions of **1** to the two first equivalents of a strong dienophile. The heats of reaction $\Delta H_r(1) = -9.5 \pm 1.2$ kcal·mol^{-1} and $\Delta H_r(2) = -7.3 \pm 1.2$ kcal·mol^{-1} for $\mathbf{1} + SO_2 \rightleftarrows \mathbf{13}$ and $\mathbf{13} + SO_2 \rightleftarrows \mathbf{14}$, respectively, are nearly the same in (D_7)DMF. The inertia of bis-sulfolene **14** toward reaction with SO_2 is attributed to the 'barrelene effect' which destabilizes the tris-sulfolene **15**, the heat of reaction $\mathbf{14} + SO_2 \rightleftarrows \mathbf{15}$ being estimated $\Delta H_r(3) > -3$ kcal·mol^{-1} in (D_7)DMF. In parallel with the tandem cheletropic additions of SO_2 to **1** and in agreement with the *Dimroth* [16] and *Bell-Evans-Polanyi* [17] principle, the lower *Diels-Alder* reactivity of bis-adducts of **1** compared with that of **1** and the corresponding mono-adducts of **1** can be attributed to the lower exothermicity of the additions of the third equivalent of dienophile compared with that of the additions of the first and second equivalent of dienophile to **1**. This is also due to the destabilizing 'barrelene effect' in the *Diels-Alder* tris-adducts of **1**.

We thank the *Swiss National Science Foundation*, the *Fonds Herbette*, Lausanne, and *F. Hoffmann-La Roche & Co. AG*, Basel, for generous financial support.

Experimental Part

General. See [33]. FC = flash chromatography. Synthesis of [2.2.2]hericene (**1**), see [1].

8,9,10,11-Tetramethylidene-4-thiatricyclo[5.2.2.0^{2,6}]undec-2(6)-ene 4,4-Dioxide (**13**). Gaseous SO_2 was bubbled through a frit in a soln. of **1** (93 mg, 0.5 mmol) in CH_2Cl_2 (10 ml) at 20°. The reaction was monitored by TLC on silica gel. The bubbling of SO_2 was stopped when **1** had disappeared. The mixture was immediately evaporated and the residue purified by FC on silica gel (40–63 mm, *Lobar A (Merck)*, CH_2Cl_2/petroleum ether 1:1): 50 mg (40%), colourless crystals. M.p. > 250° (dec.). UV (CH_3CN): 227 (14000), 248 (10500), 257 (9900), 272 (9600). IR (KBr): 2990, 1615, 1410, 1310, 1250, 1160, 1110, 900. ^{1}H-NMR (80 MHz, $CDCl_3$): 5.29 (*s*, 4 H); 4.99 (*s*, 4 H); 3.93 (*s*, 4 H); 3.85 (*s*, 2 H). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 142.3 (*s*, C(8), C(9), C(10), C(11)); 133.2 (*s*, C(2), C(6)); 105.8 (*t*, ^1J(C,H) = 160, 4 CH_2=C); 57.5 (*t*, ^1J(C,H) = 145, C(3), C(5)); 53.5 (*dm*, ^1J(C,H) = 144, C(1), C(7)). MS (70 eV): 247 (10), 246 (66, M^+), 182 (100), 167 (65), 165 (78), 152 (35), 141 (23), 128 (26), 115 (34), 91 (12), 89 (16), 77 (11).

13,14-Dimethylidene-4,10-dithiatetracyclo[5.5.2.0^{2,6}0^{8,12}]tetradeca-2(6),8(12)-diene 4,4,10,10-Tetraoxide (**14**). In a thick-walled *Pyrex* tube, **1** (95 mg, 0.52 mmol), anh. CH_2Cl_2 (2 mg) and di(*tert*-butyl)-*p*-cresol (2 mg) were degassed on the vacuum line. After cooling to –78°, under Ar, liq. SO_2 (8 ml) was introduced and the tube sealed under vacuum. After heating to 50° for 2 days, the tube was frozen and opened. The solvent and excess of

SO_2 were evaporated. 160 mg (99%), colourless solid. M.p. > 250° (dec.). UV (CH_3CN): 232 (8600). IR (KBr): 2980, 2940, 1730, 1320, 1300, 1260, 1240, 1150, 1110, 1085. ^1H-NMR (80 MHz, $CDCl_3$): 5.27 (*s*, 2 H); 5.03 (*s*, 2 H); 4.14 (*s*, H–C(1), H–C(7)); 3.94 (*s*, $CH_2(3)$, $CH_2(5)$, $CH_2(9)$, $CH_2(11)$). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 139.3 (*s*, C(13), C(14)); 134.8 (*s*, C(2), C(6), C(8), C(12)); 106.4 (*t*, ^1J(C,H) = 160, CH_2=C(13), CH_2=C(14)); 57.7 (*t*, ^1J(C,H) = 136, C(3), C(5), C(9), C(11)); 49.3 (*d*, ^1J(C,H) = 140, C(1), C(7)). MS (70 eV): 310 (1, M^+), 246 (66), 182 (72), 165 (55), 152 (26), 128 (21), 115 (29), 64 (100).

Sample Preparation for Kinetic and Thermodynamic Measurements. Gaseous SO_2 (*Fluka, puriss.*; < 0.015% H_2O) was bubbled through anh. $CDCl_3$ or (D_7)DMF. The concentration of SO_2 was determined by iodometric titration: Aliquots of 0.5 ml (*Hamilton 750-TLL* syringe) were introduced below 60 ml of H_2O, and SO_2 was titrated with 0.1N I_2. Average of at least 3 independent titrations was taken. By syringe, 0.5 ml of SO_2 soln. (10–20 equiv. of SO_2 for $CDCl_3$ soln.; 30–50 equiv. of SO_2 for (D_7)DMF soln.) were added through a septum to **1** (1–10 mg) in a 5-mm NMR tube cooled to −78° under Ar. The NMR tube was dried before *in vacuo* in a flame, the septum placed at 20°, and the tube cooled to −78°, thus establishing a depression making the injection of the SO_2 soln. easier. The NMR tube was frozen in liq. N_2, connected to the vacuum line, evacuated, and sealed. For the experiments using high concentration of SO_2, **1** and a small amount of $CDCl_3$ or (D_7)DMF were first introduced into the NMR tube. The tube was connected to the vacuum line and a known amount of SO_2 was transfered to it, and sealed under vacuum.

Evaluation of the Equilibrium Constants. Concentration of **1**, **13**, and **14** were determined by integration [34] of the 360-MHz ^1H-NMR signals (> 200 transients, 8 K memory space). Concentration of SO_2 was given by $[SO_2] = [SO_2]_0 - [\mathbf{13}] - 2[\mathbf{14}]$, where $[SO_2]_0$ is the initial concentration determined by iodometric titration. Corrections (5–20%) were made for the amount of SO_2 in the volume above the liquid for $CDCl_3$ soln., assuming ideal soln. [35] using the equation $n_v = nP_0/n_t(RTK/V + P_0/n_t)$, where n_v = number of moles of SO_2 in the gas phase, P_0 = vapor pressure [Pa] of SO_2 at temperature T[K], n_t = ideal gas constant (8.314 $J \cdot K^{-1} \cdot mol^{-1}$), K = compressibility factor of SO_2 (= 1.024 [36]), and V = gas-phase volume [m^3]. P_0 is given by $\log P_0 = (-0.2185\ A/T) + B$ [35] where A is the heat of vaporisation of SO_2 (6.3981 $kcal \cdot mol^{-1}$), B is a constant (8.115603), and T the abs. temp.

Because of the high solubility of SO_2 in (D_7)DMF [37] (167 ml SO_2/g DMF at 60°/1 atm), the SO_2 soln. in this solvent are not ideal soln., and no corrections were necessary for the amount of SO_2 in the gas phase above the liquid phase.

Rate-Constant Evaluations. The 5-mm NMR tubes were quickly warmed to the temp. (30, 60, or 80°) of the reaction (complete immersion in the water bath of the thermostat). Each measurement of the kinetics is given by another NMR tube withdrawn from the water bath and quickly cooled to 0°. The concentrations of **1**, **13**, and **14**

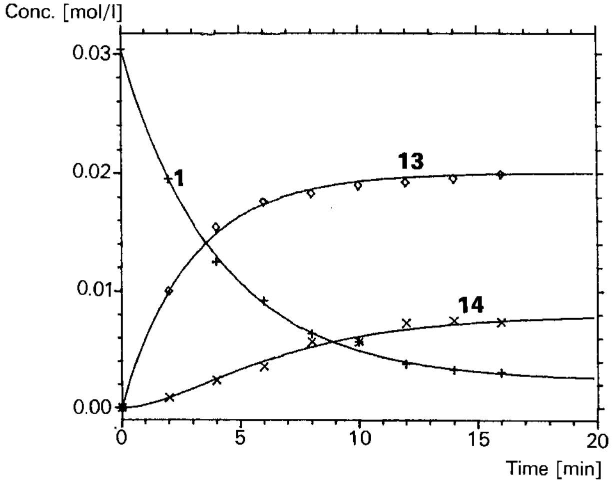


Figure. *Example of kinetic measurements for the successive cheletropic additions* **1** + $SO_2 \rightleftarrows$ **13** *and* **13** + $SO_2 \rightleftarrows$ **14** *in* *(D_7)DMF at 80°*. Each series of points (concentrations: +, □, ×) were given by an individual NMR tube. The curves were fitted by calculations using equations taken from [24].

were then measured by ^{1}H-NMR. The rate constants k_{-1} and k_{-2} of the cheletropic elimination of SO_2 were given by $k_{-1} = k_1/K_1$ and $k_2 = k_2/K_2$. The pseudo-first-order constants (40–120 equiv. of SO_2) were derived by nonlinear regressions (computer [23]) of the system of equations taken from [24].

An example of the kinetics of the tandem cheletropic addition of SO_2 to **1** is shown in the *Figure*. The kinetics were followed for at least 10 half-lives of **1** in the case of the slowest reactions (1–120 days).

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