Hetero-*Diels-Alder* and Cheletropic Additions of Sulfur Dioxide to 1,2-Dimethylidenecycloalkanes. Determination of Thermochemical and Kinetics Parameters for Reactions in Solution and Comparison with Estimates From Quantum Calculations

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Below −60° and without catalyst, 1,2-dimethylidenecyclopentane (**16**), 1,2-dimethylidenecyclohexane (**13**), 1,2-dimethylidenecycloheptane (**17**), and 1,2-dimethylidenecyclooctane (**18**) add to sulfur dioxide in the hetero-*Diels-Alder* mode, giving the corresponding sultines 4,5,6,7-tetrahydro-1*H*-cyclopent[*d*][1,2]oxathiin 3-oxide (**19**), 1,4,5,6,7,8-hexahydro-2,3-benzoxathiin 3-oxide (**14**), 4,5,6,7,8,9-hexahydro-1*H*-cyclohept[*d*][1,2]oxathiin 3-oxide (**20**), and 1,4,5,6,7,8,9,10-octahydrocyclooct[*d*][1,2]oxathiin 3-oxide (**21**), respectively. Above −40°, the sultines are isomerized into the corresponding sulfolenes 3,4,5,6-tetrahydro-1*H*-cyclopenta[*c*]thiophene 2,2-dioxide (**22**), 1,3,4,5,6,7-hexahydrobenzo[*c*]thiophene 2,2-dioxide (**15**), 3,4,5,6,7,8-hexahydro-1*H*-cyclohepta[*c*]thiophene 2,2-dioxide (**23**), and 1,3,4,5,6,7,8,9-octahydrocycloocta[*c*]thiophene 2,2-dioxide (**24**). Kinetics and thermodynamics data were collected for these reactions. The sultines are *ca.* 10 kcal/mol *Diels-Alder* additions ($\Delta H^{\neq}(\mathbf{16} + SO_2 \rightarrow \mathbf{19}) = 6.6 \pm 0.2$ kcal mol^{-1} and $\Delta H^{\neq}(\mathbf{13} + SO_2 \rightarrow \mathbf{14}) = 7.2 \pm 0.4$ kcal mol^{-1}) are *ca.* 2 kcal smaller than the activation enthalpies of the corresponding cheletropic additions. The activation entropies of the hetero-*Diels-Alder* additions ($\Delta S^{\neq}(\mathbf{16} + SO_2 \rightarrow \mathbf{19}) = -50.3 \pm 1.1$ cal mol^{-1} K^{-1} and $\Delta S^{\neq}(\mathbf{13} + SO_2 \rightarrow \mathbf{14}) = -48.7 \pm 1.8$ cal mol^{-1} K^{-1}) are more negative than the corresponding reaction entropies ($\Delta S_r(\mathbf{16} + SO_2 \rightleftharpoons \mathbf{19}) = -40.9 \pm 1.5$ cal mol^{-1} K^{-1} and $\Delta S_r(\mathbf{13} + SO_2 \rightleftharpoons \mathbf{14}) = -36 \pm 3$ cal mol^{-1} K^{-1}) in agreement with third-order rate laws that imply that two molecules of SO_2 intervene in the transition states of these cycloadditions. Similar observations were made for the cheletropic additions of SO_2. Attempts to simulate the thermodynamics and kinetics parameters of the reactions of SO_2 with dienes **16** and **13** by density-functional theory (DFT) suggest that the calculations require an appropriate number of polarization functions in the basis set employed. A satisfactory recipe to compute the SO_2 additions to large dienes can be: B3LYP/6-31G(d) geometry optimizations followed by B3LYP/6-31 + G(2df,p) single-point calculations or G2(MP2,SVP) estimates on the B3LYP/6-31G(d) geometries.

1. Introduction. – The cheletropic reaction $({}_{\omega}2_s + {}_{\pi}4_s)$ [1] of SO_2 with 1,3-dienes to give 2,5-dihydrothiophene 1,1-dioxides (sulfolenes) has been known since 1914 [2][3]. Although selenium dioxide [4], *N*-sulfinylamines [5] (RN=S=O), and sulfines (RR′C=S=O) [6][7], which have considerable structural analogy to SO_2, readily take part in hetero-*Diels-Alder* additions [8], the $[{}_{\omega}2_s + {}_{\pi}4_s]$-cycloaddition of SO_2 to 1,3-dienes was a rare reaction described for two cases of extremely reactive 1,3-dienes, *i.e.*,

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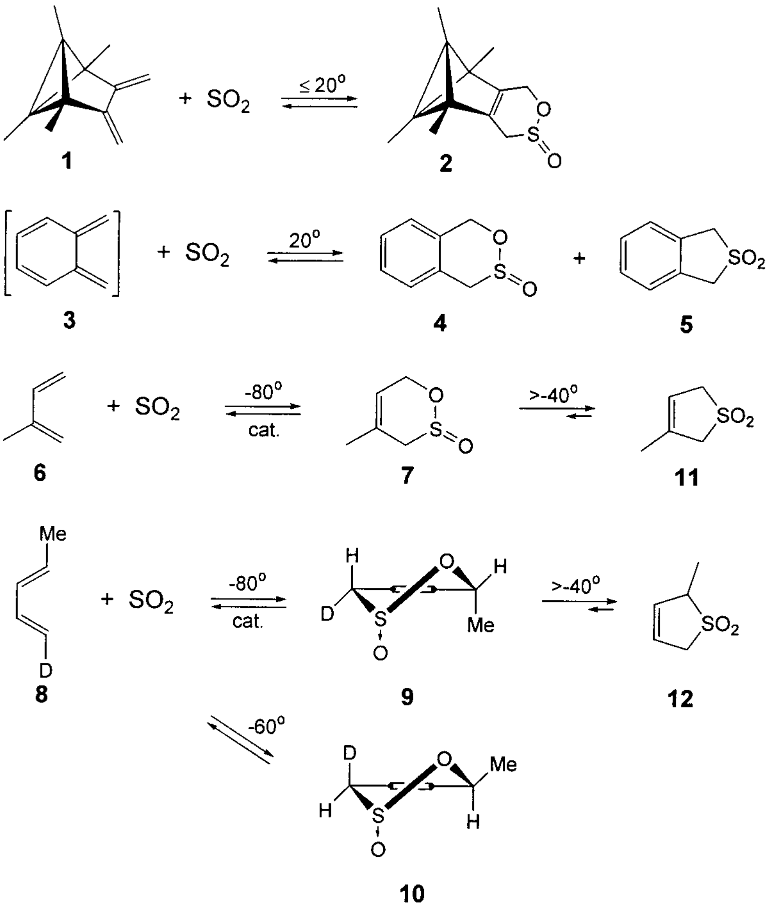
1 + SO_2 → **2** [9] and **3** + SO_2 → 4 + 5 [10] 2) (*Scheme 1*). In 1992, we reported that simple dienes, such as isoprene (**6**) and (*E*,*E*)-(1-D_1)piperylene (= (*E*,*E*)-(1-D_1)penta-1,3-diene; **8**), react reversibly with SO_2 at low temperature and in the presence of a suitable protic or *Lewis* acid catalyst giving the corresponding sultines (= 3,6-dihydro-1,2-oxathiin 2-oxides) **7** and **9** + **10**, respectively [11]. Above −50°, the sultines **7**, **9**, and **10** undergo fast cycloreversion liberating the starting diene and SO_2 that can undergo cheletropic addition [1–3] above −40° to give the corresponding sulfolenes **11** and **12**, respectively (*Scheme 1*). The results with deuterated piperylene **8** led us to conclude that the hetero-*Diels-Alder* additions of SO_2 are suprafacial (*Woodward-Hoffmann* rules [1]) and follow the *Alder endo*-stereoselectivity rule [12]3). These observations led us to invent a new C–C bond-forming reaction in which electron-rich dienes are

Scheme 1



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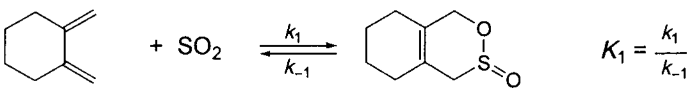
2) See also the reactions of S_2 to 1,3-dienes [7].

3) See the reactions of sulfur dioxide bis(imides) (= sulfur diimides) [8].

condensed with electron-rich alkenes and SO_2, giving sulfinic derivatives that can undergo stereoselective *retro*-ene elimination of SO_2 providing polypropanoate fragments containing up to three new stereogenic centers and an (*E*)-alkenic unit, on one hand [13a], or that can react with electrophiles giving the corresponding sulfones, on the other hand [13b,c]. An asymmetric version of this one-pot four-component synthesis of sulfones has been presented recently [14].

We have found that 1,2-dimethylidenecyclohexane (**13**), which is one of the most reactive 2,3-dialkylidiene in a *Diels-Alder* cycloaddition [15], adds reversibly to SO_2 at 187 K without catalyst, generating sultine **14** nearly quantitatively [16] (*Scheme 2*). This observation has allowed us to determine the rate law (*Eqn. 1*) of the uncatalyzed hetero-*Diels-Alder* addition of sulfur dioxide to diene **13** at 198 K. It confirmed a prediction based on high-level *ab initio* quantum calculations for the reaction of SO_2 with butadiene that two molecules of SO_2 are involved in the transition state of their hetero-*Diels-Alder* addition. A similar prediction was suggested for the cheletropic addition of SO_2 to butadiene and confirmed by the rate law (*Eqn. 2*) found experimentally for the cheletropic addition of SO_2 to diene **13** to give sulfolene **15** [16] (*Scheme 3*).

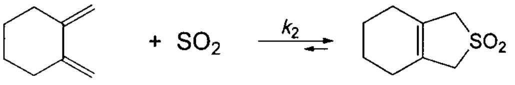
Scheme 2



13 **14**

$$\frac{d[\mathbf{14}]}{dt} = k_1[\mathbf{13}]\,[SO_2]^2 - k_{-1}[\mathbf{14}]\,[SO_2] \text{ at 198 K} \qquad (1)$$

Scheme 3

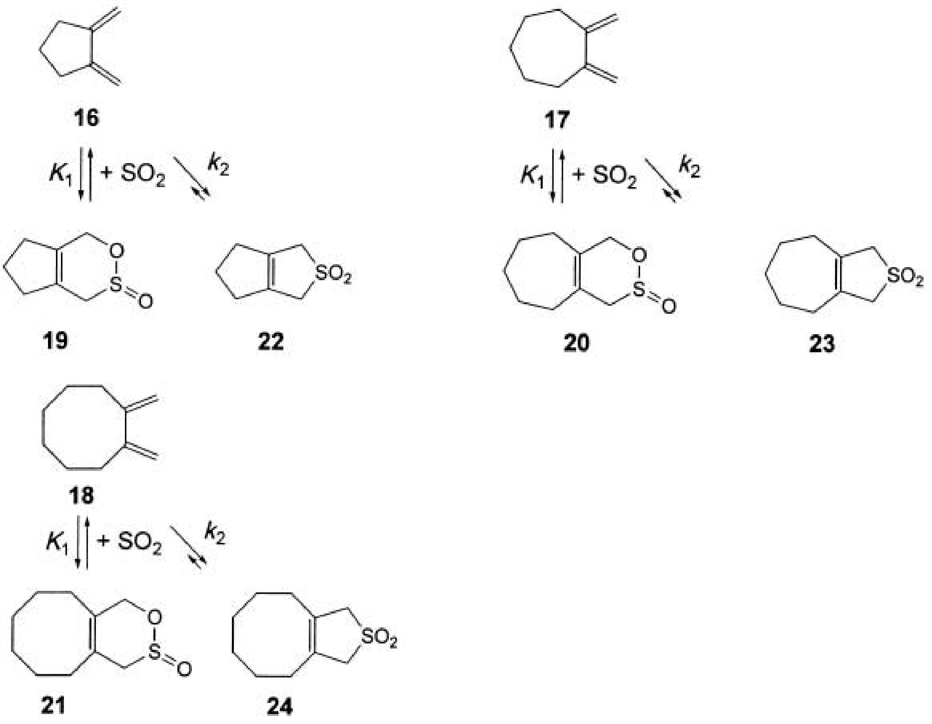


13 **15**

$$\frac{d[\mathbf{15}]}{dt} = k_2\,[\mathbf{13}]\,[SO_2]^2 \text{ at 261.2 K} \qquad (2)$$

In this report, we determined the thermochemical and activation parameters for the hetero-*Diels-Alder* additions of sulfur dioxide to diene **13**. We measured also the equilibrium constants for the hetero-*Diels-Alder* additions of SO_2 to 1,2-dimethylidenecyclopentane (**16**), to 1,2-dimethylidenecycloheptane (**17**), and to 1,2-dimethylidenecyclooctane (**18**) that give the corresponding sultines **19**–**21** (*Scheme 4*). We evaluated the rate constants of these cycloadditions and those for the cheletropic addition of SO_2 to **16**–**18** that give the corresponding sulfolenes **22**–**24**. The data show that the sulfolenes are *ca.* 10 kcal/mol more stable than their isomeric sultines. The activation entropy of the hetero-*Diels-Alder* addition $\mathbf{13} + SO_2 \rightleftharpoons \mathbf{14}$ and $\mathbf{16} + SO_2 \rightleftharpoons \mathbf{19}$ compared with the corresponding entropies of reaction confirm that the transition state

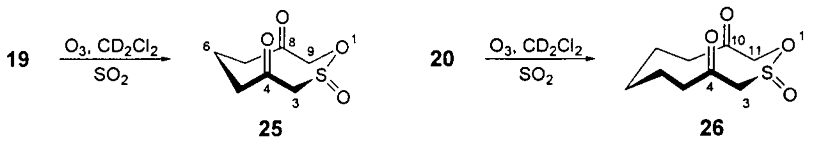
Scheme 4



of these cycloadditions is more ordered than the adduct in CH_2Cl_2/SO_2 mixtures, in agreement with the hypothesis that two molecules of SO_2 are intervening in the transition states of these reactions [16].

Thermodynamics Data. – Dienes **13** and **16**–**18** were prepared according to the procedures of *Bickelhaupt* and co-workers [17]. The structures of sultines **14** and **19**–**21** and of sulfolenes **15** and **22**–**24** were given by their spectral data (*Exper. Part*) and, in the cases of **14** and **15**, by their products of ozonolysis [18]. The new sultines **19** and **20** were also submitted to ozonolysis and generated the unstable diones **25** and **26**, respectively, that were characterized by their spectral data (*Scheme 5*).

Scheme 5

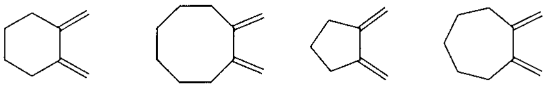


The equilibrium constants $K_1(\mathbf{13} + SO_2 \rightleftharpoons \mathbf{14})$ for the hetero-*Diels-Alder* addition of SO_2 to **13** were measured at 219 ± 1, 250.7 ± 1, and 261.2 ± 1 K and found to be 11.3 ±

0.9, 1.07 ± 0.05, and 0.38 ± 0.05 $dm^3 mol^{-1}$, respectively (see *Exper. Part*). The *Van't Hoff* plot furnished $\Delta H_r(\mathbf{13} + SO_2 \rightleftharpoons \mathbf{14}) = -8.9 \pm 0.8$ kcal mol^{-1} and $\Delta S_r(\mathbf{13} + SO_2 \rightleftharpoons \mathbf{14}) = -36 \pm 3$ cal mol^{-1} K^{-1}, with a correlation coefficient of 0.9959.

The equilibrium constants $K_1(\mathbf{16} + SO_2 \rightleftharpoons \mathbf{19}) = 31.0 \pm 1.3$, 15.8 ± 3.4, 12.1 ± 0.7, 0.41 ± 0.05, 0.20 ± 0.03, and 0.068 ± 0.005 $dm^3 mol^{-1}$ were measured at 187.5, 191.7, 198.0, 229.6, 240.1, and 250.7 ± 1 K, respectively. This gave for the hetero-*Diels-Alder* additions of SO_2 to **16** thermochemical parameters ($\Delta H_r(\mathbf{16} + SO_2 \rightarrow \mathbf{19}) = -9.0 \pm 0.3$ kcal mol^{-1} and $\Delta S_r(\mathbf{16} + SO_2 \rightleftharpoons \mathbf{19}) = -40.9 \pm 1.5$ cal mol^{-1} K^{-1}, with a correlation coefficient of 0.99703.

For the hetero-*Diels-Alder* additions of SO_2 to **17** and **18** at −75° (198 K), equilibrium constants $K_1(\mathbf{17} + SO_2 \rightleftharpoons \mathbf{20}) = 1.9 \pm 0.4$ $dm^3 mol^{-1}$ and $K_1(\mathbf{18} + SO_2 \rightleftharpoons \mathbf{21}) = 22 \pm 9$ $dm^3 mol^{-1}$ were obtained by measuring the rate constants of the cycloadditions and cycloreversion at 198 K ($K_1 = k_1/k_{-1}$, see below). These data show (*Fig. 1*) that the three [4 + 2] cycloadditions of SO_2 to dienes **13**, **16**, and **18** have similar thermodynamical characteristics, as expected for equilibria in which cycloaddents and corresponding adducts have similar ring strains [19].



13 **18** **16** **17**

K_1^{198K}(diene + $SO_2 \rightleftharpoons$ sultine): 85.7 ± 2.3 22 ± 9 12.1 ± 0.7 1.9 ± 0.4

Fig. 1. *Equilibrium constants* K_1 [dm^3mol^{-1}] *for the hetero-*Diels-Alder *addition of* SO_2 *to 1,2-dimethylidenecycloalkanes*

Apparently, diene **17** equilibrates with sultine **20** with an equilibrium constant K_1 *ca.* 10 times smaller than for the other hetero-*Diels-Alder* additions at 198 K, suggesting an increase of ring strain of *ca.* 1 kcal/mol going from **17** to sultine **20**.

Kinetics Data. – In a preliminary communication [16], we have shown that the hetero-*Diels-Alder* addition $\mathbf{13} + SO_2 \rightleftharpoons \mathbf{14}$ follows the rate law of *Eqn. 1* and that the cheletropic addition $\mathbf{13} + SO_2 \rightleftharpoons \mathbf{15}$ follows the rate law of *Eqn. 2* at 198 K (see *Schemes 2* and *3*). We found now that the same rate laws apply also at higher temperatures (261 K) at which diene **13** equilibrates with sultine **14** and generates sulfolene **15** irreversibly (see *Table 1*, *Figs. 2* and *3*). Furthermore, all kinetics data, including those for temperature-jump experiments in which sultine **14** formed at low temperature (198 K) was heated suddenly to 261 K, are consistent with a scheme of two parallel reactions in which the sultine **14** undergoes equilibration with diene $\mathbf{13} + SO_2$ before forming the sulfolene **15**. The data could also be fitted by a model in which sulfolene **15** arises from direct rearrangement of sultine **14** [20], although *ab initio* calculations showed that such a mechanism can be disregarded [21].

Kinetics measurements at various temperatures for the hetero-*Diels-Alder* reaction $\mathbf{13} + SO_2 \rightleftharpoons \mathbf{14}$ gave third-order rate constants $10^6 \cdot k_1 = 0.43 \pm 0.08$, 1.01 ± 0.08, 3.03 ± 0.17, 4.75 ± 0.17, 86 ± 8, and 110 ± 8 at 187.5, 198.0, 208.5, 219.1, 250.7, and 261.2 ± 1 K,

Table 1. *Apparent Pseudo-First-Order Rate Constants* k'$_1$(**13** + SO_2 → **14**), k'$_{-1}$(**14** → **13** + SO_2), *and* k'$_2$(**13** + SO_2 → **15**) *as a Function of* SO_2 *Concentration at* $-12°$ (261 K) [a])

	$[SO_2]$[mol dm^{-3}]									
	2.66	3.19	4.68	8.60	9.55	12.64	13.02	15.16	15.46	16.46
$k'_1 \cdot 10^3[s^{-1}]$	1.08 ± 0.22	2.15 ± 0.18	2.4 ± 0.6	6.9 ± 2.3	13.5 ± 1.3	11.4 ± 1.0	11.9 ± 1.1	32.4 ± 3.8	27 ± 10	29.8 ± 6.4
$k'_{-1} \cdot 10^3[s^{-1}]$	2.2 ± 0.4	2.8 ± 0.2	2.5 ± 0.6	2.0 ± 0.6	3.1 ± 0.3	2.1 ± 0.2	2.1 ± 0.2	3.7 ± 0.5	1.4 ± 0.2	3.4 ± 0.8
$k'_2 \cdot 10^3[s^{-1}]$	0.200 ± 0.004	0.242 ± 0.014	0.331 ± 0.014	1.17 ± 0.06 [b])	1.24 ± 0.05	1.84 ± 0.08	1.87 ± 0.13	2.89 ± 0.14	5.7 ± 2.3 [b])	2.66 ± 0.26 [b])

[a]) By ^{1}H-NMR (30° pulses, toluene as internal reference, see *Exper. Part*). Initial concentration ratio $[SO_2]/[\mathbf{13}] > 8$. [b]) Less-precise values were not used for the SO_2 partial reaction order determination.

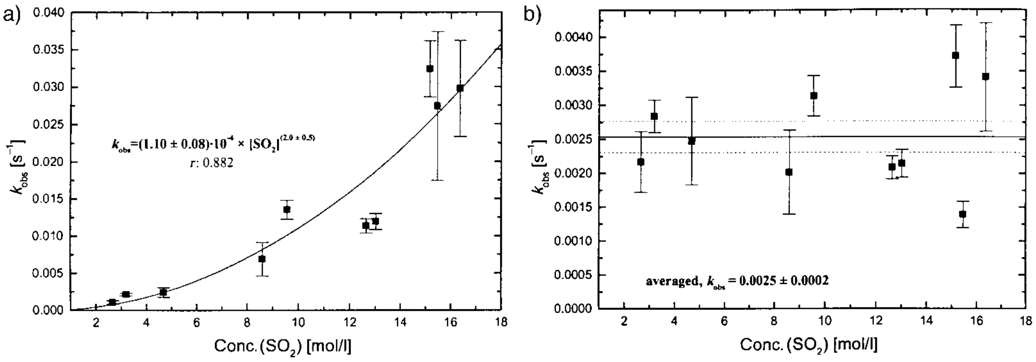


Fig. 2. *Determination of the order of the rate law of* a) *the hetero*-Diels-Alder *addition* **13** + SO_2 → **14** ($k_{obs} = k_1^{obs}[SO_2]^x = k'_1$) *and of* b) *the cycloreversion* **14** → **13** + SO_2 *at 261 K* ($k'_{obs} = k_{-1}[SO_2] = k'_{-1}$)

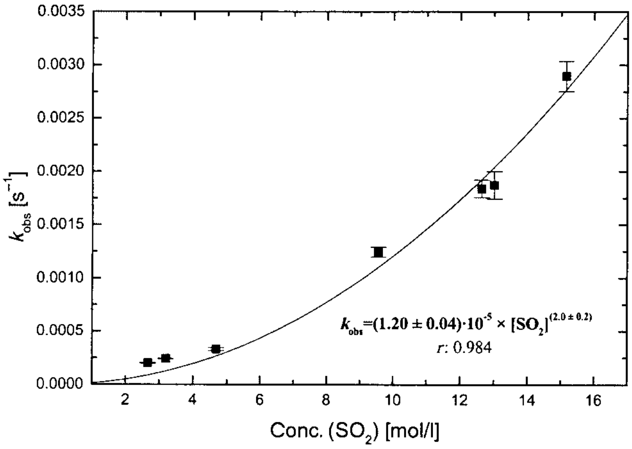


Fig. 3. *Determination of the order of the rate law of the cheletropic addition* **13** + SO_2 → **15** *at 261 K* ($k_{obs} = k_2^{obs}[SO_2]^x = k'_2$)

respectively. The *Arrhenius* plot yields $\ln A = 5.7 \pm 0.9$ and $E_a = 7.7 \pm 0.4$ kcal mol^{-1}, and the *Eyring* plot provides $\Delta S^{\neq} = -48.7 \pm 1.8$ cal mol^{-1} K^{-1} and $\Delta H^{\neq} = 7.2 \pm 0.4$ kcal mol^{-1}.

Table 2. *Examples of Kinetic Data for the Hetero-*Diels-Alder *Addition* $\mathbf{16} + SO_2 \rightarrow \mathbf{19}$ (k'_1, k_1), *the Cycloreversion* $\mathbf{19} + SO_2 \rightarrow \mathbf{16}$ (k'_{-1}, k_{-1}), *and the Cheletropic Addition* $\mathbf{16} + SO_2 \rightarrow \mathbf{22}$ (k'_2, k_2)

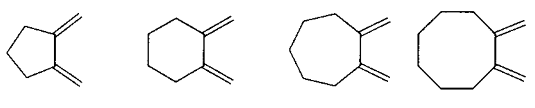
T[K] (± 1)	$[\mathbf{16}]_o$ a) [mol dm^{-3}]	$[SO_2]_o$ [mol dm^{-3}]	$k'_1 \cdot 10^6$ [s^{-1}]	$k_1 \cdot 10^6$ b) [dm^6 mol^{-2} s^{-1}]	$k'_{-1} \cdot 10^6$ c) d) [s^{-1}]	$k'_2 \cdot 10^6$ [s^{-1}]	$k_2 \cdot 10^6$ e) [dm^6 mol^{-2} s^{-1}]
187.5	0.370 ± 0.001	7.15 ± 0.10	41.6 ± 0.1	0.81 ± 0.02		1.17 ± 0.03	0.0229 ± 0.0007
191.7	0.405 ± 0.001	8.20 ± 0.12	79.4 ± 0.4	1.18 ± 0.02	0.61 ± 0.13	1.84 ± 0.09	0.0274 ± 0.0015
198.0	0.233 ± 0.001	4.66 ± 0.07	48.2 ± 0.3			1.28 ± 0.17	
	0.313 ± 0.001	11.39 ± 0.16	254 ± 1	2.09 ± 0.04	1.75 ± 0.17	7.72 ± 0.14	0.059 ± 0.005
229.6	0.331 ± 0.001	6.85 ± 0.10	1520 ± 140	32.3 ± 3.1	540 ± 50	78.4 ± 0.9	1.67 ± 0.04
240.1	0.290 ± 0.001	10.93 ± 0.15	6200 ± 800	52 ± 7	2900 ± 300	439 ± 3	3.68 ± 0.08
250.7	0.370 ± 0.001	7.75 ± 0.11	4700 ± 200	78 ± 4	8900 ± 400	584 ± 4	9.7 ± 0.2

a) Average deviation for several weighings. b) $\ln A = 4.8 \pm 0.5$, $E_a = 7.0 \pm 0.2$ kcal mol^{-1}; $\Delta H^{\ddagger} = 6.6 \pm 0.2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -50.3 \pm 1.1$ cal mol^{-1} K^{-1}. c) $k_{-1} = k'_{-1}$. d) $\ln A = 27.3 = 0.7$, $E_a = 15.9 \pm 0.2$ kcal mol^{-1}; $\Delta H^{\ddagger} = 15.5 \pm 0.3$ kcal mol^{-1}, $\Delta S^{\ddagger} = -5.6 \pm 1.4$ cal mol^{-1} K^{-1}. e) $\ln A = 6.7 \pm 0.6$, $E_a = 9.1 \pm 0.2$ kcal mol^{-1}; $\Delta H^{\ddagger} = 8.7 \pm 0.2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -46.5 \pm 1.1$ cal mol^{-1} K^{-1}.

The kinetics data for the reactions of SO_2 with 1,2-dimethylidenecyclopentane (**16**) are summarized in *Table 2*. For both hetero-*Diels-Alder* additions $\mathbf{13} + SO_2 \rightarrow \mathbf{14}$ and $\mathbf{16} + SO_2 \rightarrow \mathbf{19}$, very similar activation enthalpies ($\Delta H^{\ddagger}(\mathbf{13} + SO_2 \rightarrow \mathbf{14}) = 7.2 \pm 0.4$ kcal mol^{-1}, $\Delta H^{\ddagger}(\mathbf{16} + SO_2 \rightarrow \mathbf{19} = 6.6 \pm 0.2$ kcal mol^{-1}) and activation entropies ($\Delta S^{\ddagger}(\mathbf{13} + SO_2 \rightarrow \mathbf{14}) = -48.7 \pm 1.8$ cal mol^{-1} K^{-1}, $\Delta S^{\ddagger}(\mathbf{16} + SO_2 \rightarrow \mathbf{19}) = -50.3 \pm 1$ cal mol^{-1} K^{-1}) are found. Both cycloadditions must have transition states that are more ordered than their adducts (sultines) in solution since the activation entropies are *ca.* 10 e.u. more negative than their reaction entropies ($\Delta S_r(\mathbf{13} + SO_2 \rightleftharpoons \mathbf{14}) = -36 \pm 3$ cal mol^{-1} K^{-1}, $\Delta S_r(\mathbf{16} + SO_2 \rightleftharpoons \mathbf{19}) = -40.9 \pm 1.5$ cal mol^{-1} K^{-1}), consistently with rate laws (*Eqn. 1*) that imply two molecules of SO_2 in the transition states of these cycloadditions. Alternatively, one can envisage differential solvation effects that gives rise to *Diels-Alder* transition states that are better solvated by SO_2 than the corresponding reactants (diene + SO_2) and products (sultines). The activation parameters $\Delta H^{\ddagger}(\mathbf{19} \rightarrow \mathbf{16} + SO_2) = 15.5 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\ddagger}(\mathbf{19} \rightarrow \mathbf{16} + SO_2) = -5.6 \pm 1.4$ cal mol^{-1} K^{-1} measured for the cycloreversion of sultine **19** into diene **16** and SO_2 show a negative entropy of activation for a dissociative process, thus confirming a stronger solvation of the *Diels-Alder* transition states compared with the sultine.

We determined the activation parameters (*Table 2*) for the cheletropic addition of SO_2 to 1,2-dimethylidenecyclopentane under our conditions, *i.e.*, with a large excess of SO_2. The data obtained ($\Delta H^{\ddagger}(\mathbf{16} + SO_2 \rightarrow \mathbf{22}) = 8.7 \pm 0.2$ kcal mol^{-1}, $\Delta S^{\ddagger}(\mathbf{16} + SO_2 \rightarrow \mathbf{22}) = -46.5 \pm 1.1$ cal mol^{-1}K^{-1}) do not differ significantly from those reported by *Isaacs* and *Laila* [22] and measured at higher temperatures (25 or 40°) under pseudo-first-order conditions in the presence of a large excess of diene **16** ($\Delta H^{\ddagger} \cong 7.0$ kcal mol^{-1}, $\Delta S^{\ddagger} \cong -53$ cal mol^{-1}K^{-1} [22]).

Comparison of the rate constants k_1 does not show significant reactivity differences for the hetero-*Diels-Alder* additions of SO_2 to **13**, **16**, **17**, and **18** at 198 K (*Fig. 4*; see also *Table 3*). The slowest diene is **17**, which gives the smallest equilibrium constant for the hetero-*Diels-Alder* addition of SO_2.



	16	**13**	**17**	**18**
k_1 (diene + $SO_2 \rightarrow$ sultine) 10^6: at 198 K [$dm^6 mol^{-2} s^{-1}$]	2.09 ± 0.04	1.01 ± 0.08	0.52 ± 0.01	3.95 ± 0.08
k_{rel}:	4.2	1.9	(1.0)	7.7
k_2 (diene + $SO_2 \rightarrow$ sulfolene) 10^8: at 198 K [$dm^6 mol^{-2} s^{-1}$]	5.9 ± 0.5	3.29 ± 0.37	1.87 ± 0.09	18.9 ± 0.5
k_{rel}:	3.3	1.8	(1.0)	10

Fig. 4. *Rate constants* k_1 *and* k_2 [$dm^6 mol^{-2} s^{-1}$] *for sultine and sulfolene formation, respectively, on addition of* SO_2 *to 1,2-dimethylidenecycloalkanes*

Table 3. *Kinetics Data for the Reactions of* SO_2 *with Dienes* **17** *and* **18**

Temp.	k_1 [$dm^6 mol^{-2} s^{-1}$]	k_{-1} [s^{-1}]	k_2 [$dm^6 mol^{-2} s^{-1}$]
	17 + $SO_2 \rightarrow$ **20**	**20** + $SO_2 \rightarrow$ **17**	**17** + $SO_2 \rightarrow$ **23**
198 K	$(0.52 \pm 0.01) \cdot 10^{-6}$	$(2.6 \pm 0.2) \cdot 10^{-7}$	$(1.87 \pm 0.09) \cdot 10^{-8}$
235 K	$(7.2 \pm 1.7) \cdot 10^{-6}$	$(1.8 \pm 0.4) \cdot 10^{-3}$	$(80.8 \pm 2.1) \cdot 10^{-8}$
	18 + $SO_2 \rightarrow$ **21**	**21** + $SO_2 \rightarrow$ **18**	**18** + $SO_2 \rightarrow$ **24**
198 K	$(3.95 \pm 0.08) \cdot 10^{-6}$	$(1.6 \pm 0.1) \cdot 10^{-7}$	$(1.89 \pm 0.05) \cdot 10^{-7}$

For the cheletropic additions, one finds also small reactivity differences (*Fig. 4* and *Table 3*). The slowest diene is again **17**, and the fastest is **18**. Perhaps a delicate interplay of differential ring-strain changes between dienes and the corresponding sulfolenes (*Dimroth* principle [23], *Bell-Evans-Polanyi* law [24]) and differences in flexibility between seven- and eight-membered rings can be invoked to interpret the results. Interestingly, the reactivity trends are the same for the hetero-*Diels-Alder* and cheletropic additions of sulfur dioxide.

Discussion. – In the gas phase, SO_2 generates a dimer with a binding energy amounting to *ca.* 3 kcal/mol [25]. Butadiene is known to form a *Van der Waals* complex with SO_2 with a binding energy of 3.24 ± 0.48 kcal mol^{-1} [26]. Considering the heat of reaction evaluated for the cheletropic addition **16** + $SO_2 \rightarrow$ **19** of – 19.4 kcal mol^{-1} [22], our data allow one to build the enthalpy diagram of *Fig. 5* for the reactions of SO_2 with 1,2-dimethylidenecyclopentane. Similar enthalpy diagrams should apply to the reactions of SO_2 with the other dienes **13**, **17**, and **18**. Sultines and sulfolenes are also solvated by SO_2, the extent of which in terms of relative stability of diene, sultine, and sulfolene still needs to be assessed. The difference of *ca.* 10 kcal mol^{-1} obtained between the heat of formation of sultine **14** and sulfolene **15** represents a first approximation of the difference in heat of formation between sulfones and isomeric alkyl sulfinates. No thermochemical data is available for sulfinic acid derivatives [27],

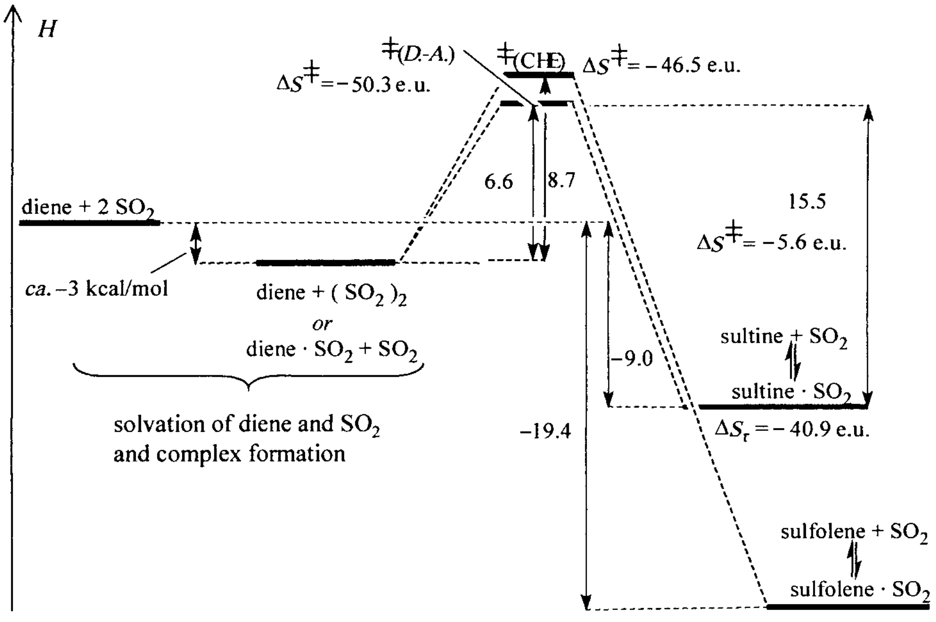


Fig. 5. *Enthalpy diagram for the additions of* SO_2 *to 1,2-dimethylidenecyclopentane* (**16**) *giving sultine* **19** *and sulfolene* **22**

although the sulfinate → sulfone rearrangement is a very well-studied reaction [28] known since 1917 [29]. The driving force for this rearrangement is the strong S=O bond in the sulfonyl group [30].

Computational Methods. – The density functional theory (DFT) was used to study the hetero-*Diels-Alder* and cheletropic reactions of buta-1,3-diene, 1,2-dimethylidenecyclopentane (**16**), and 1,2-dimethylidenecyclohexane (**13**) with SO_2. *Merz* and co-workers [31] have shown recently that DFT represents an economical alternative to obtain accurate information for organic and organometallic systems. Particularly, *Houk* and co-workers [32] studied the model *Diels-Alder* reaction between butadiene and ethene, concluding that the DFT method makes correct predictions on the relative energies and isotope effects for both the concerted and stepwise mechanisms. From the various functionals available, we have chosen the *Becke* 3-parameter exchange functional [33] and the correlation functional of *Lee-Yang-Parr* [34] (B3LYP), as there is accumulated evidence showing that B3LYP is the DFT functional exhibiting the best performance [35].

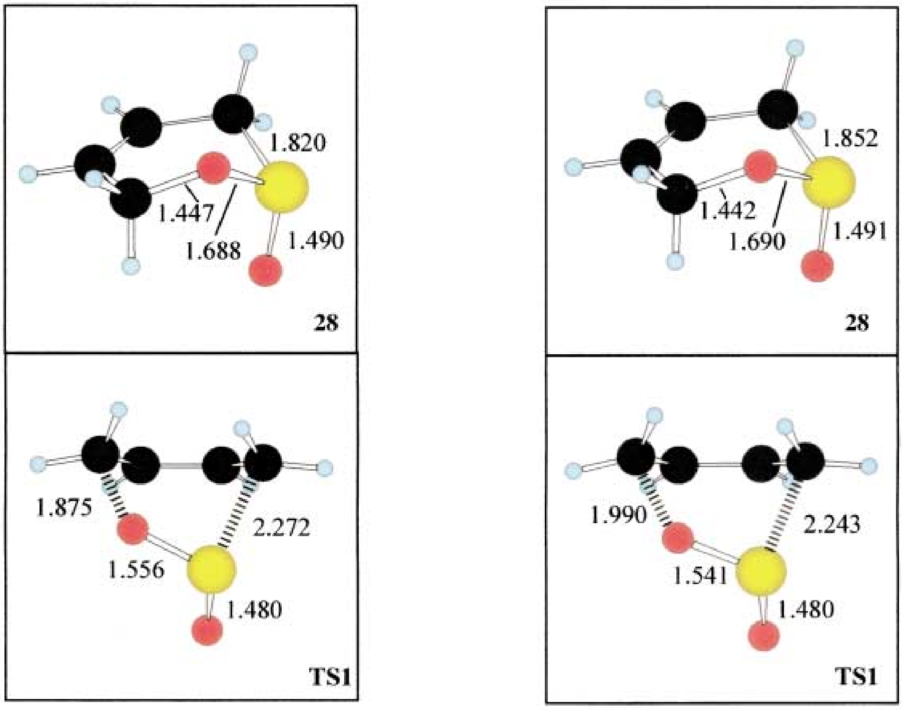
As shown [36], polarization functions play a decisive role on the energetics of reactions involving hypervalent species, such as sultines and sulfolenes. Therefore, B3LYP/6-31 + G(2df,p) and B3LYP/6-311 + G(3df,2pd) single-point calculations on the B3LYP/6-31G(d) geometries were carried out. Further refined energetic predictions were obtained by means of the G2(MP2,SVP) theory [37][38] with B3LYP geometries (it will be shown below that, for the kind of systems under study, the

MP2 and B3LYP geometries are basically equivalent). This latter level has proved to render quite accurate results on systems similar to the ones studied in the present work [39].

The thermodynamic functions (ΔH, ΔS, and ΔG) were estimated within the ideal-gas, rigid-rotor, and harmonic-oscillator approximations [40], as implemented in Gaussian 98 [41], which was the package of programs used to carry out all the calculations reported in this work. A temperature of 198 K and a pressure of 1 atm were assumed.

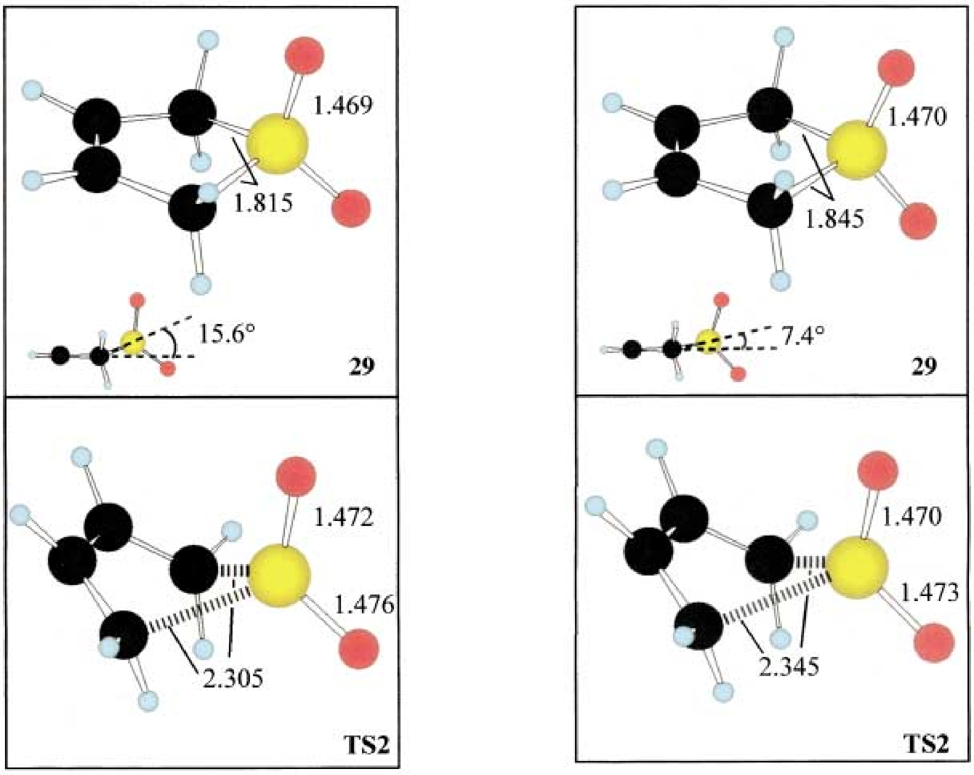
The B3LYP/6-31G(d) transition structures **TS1**–**TS6** and products (sultines and sulfolenes) corresponding to the reactions between buta-1,3-diene (**27**), 1,2-dimethylidenecyclopentane (**16**), 1,2-dimethylidenecyclohexane (**13**) and SO_2 are depicted in *Figs. 6–11*. In the case of the **27** + SO_2 reaction, the MP2/6-31G(d) geometries are also included for comparison purposes. The computed relative electronic energies for all the structures are collected in *Table 4*, and the reaction enthalpies, entropies, and *Gibbs* free energies are presented in *Table 5*. In this latter table, the experimental estimates for the thermodynamic functions are also included when available.

Figs. 6 and *7* show that the MP2/6-31G(d) and B3LYP/6-31G(d) optimized geometries of sultine **28**, sulfolene **29**, and transition structures **TS1** and **TS2** are



MP2 **B3LYP**

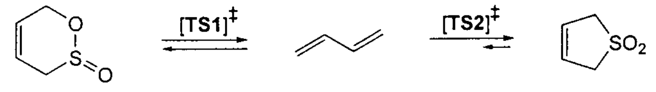
Fig. 6. *MP2/6-31G(d) andB3LYP/6-31G(d) transition structure* **TS1** *and sultine* **28** *corresponding to the hetero-*Diels-Alder *reaction of buta-1,3-diene* (**27**) *and* SO_2



MP2 **B3LYP**

Fig. 7. *MP2/6-31G(d) and B3LYP/6-31G(d) transition structure* **TS2** *and sulfolene* **29** *corresponding to the cheletropic reaction of buta-1,3-diene* (**27**) *and* SO_2

Scheme 6



28 **27** **29**

practically the same. From *Table 4* we learn that the B3LYP energies are somewhat lower than the corresponding MP2 values. However the MP2/6-31G(d)/B3LYP/6-31G(d) relative energies basically reproduce the MP2/6-31G(d) values. This demonstrates that the use of the *economical* DFT method to optimize geometries, followed by MP2//DFT single-point calculations to estimate the energetics, could be an appropriate strategy to deal with reactions of SO_2 with dienes that are larger than buta-1,3-diene and for which the MP2 optimizations become impractical.

Table 4 shows also that calculations at the B3LYP/6-31G(d) level predict the kinetic product of the **27** + SO_2 reaction to be **28** (**TS1** is lower in energy than **TS2**) and the relative energies of the sulfolene **29** and sultine **28** suggest that the latter is more stable,

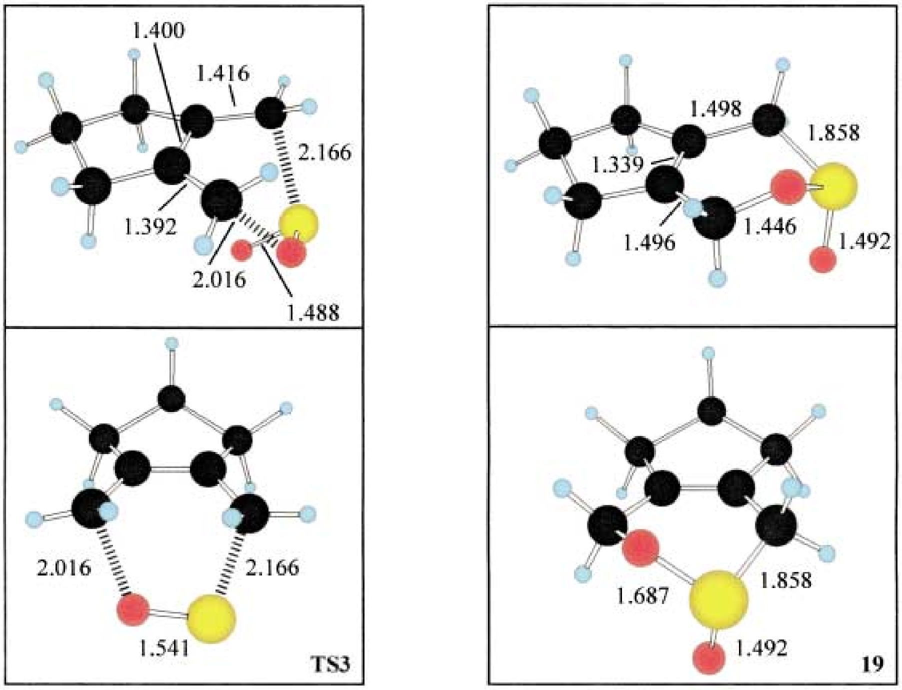


Fig. 8. *B3LYP/6-31G(d) transition structure* **TS3** *and sultine* **19** *corresponding to the hetero-*Diels-Alder *reaction of 1,2-dimethylidenecyclopentane* (**16**) *and SO_2*

Table 4. *Electronic Energies* [kcal mol^{-1}] *Relative to Reactants* (diene + SO_2) *for the Transition Structures* **TS** *and Products of the Cheletropic* (CHE) *and Hetero-*Diels-Alder (*D.-A.*) *Reactions between Buta-1,3-diene* (**27**), *1,2-Dimethylidenecyclopentane* (**16**), *or 1,2-Dimethylidenecyclohexane* (**13**) *and SO_2 Giving the Corresponding Sulfolenes* (**29**, **22**, **15**) *and Sultines* (**28**, **19**, **14**)

System	Structures	B3LYP/ 6-31G(d)	MP2/ 6-31G(d) [a])	MP2/6-31G(d//B3LYP/ 6-31G(d)	B3LYP/6-31+G(2df,p)/B3LYP/ 6-31G(d)	B3LYP/6-311+G(3df,2pd)// B3LYP/6-31G(d)	G2(MP2,SVP) [b])
27 + SO_2	**TS1** (*D.-A.*)	13.5	17.8	17.9	17.6	18.9	19.9
	28 (*D.-A.*)	−7.4	−3.8	−3.6	−0.2	2.6	−0.4
	TS2 (CHE)	18.1	19.6	19.4	19.6	20.1	19.7
	29 (CHE)	−4.3	−5.4	−5.1	−3.8	−4.4	−8.6
16 + SO_2	**TS3** (*D.-A.*)	6.9		10.0	11.3	12.5	11.8
	19 (*D.-A.*)	−11.8		−8.9	−4.5	−2.6	−4.8
	TS4 (CHE)	13.1		13.0	14.6	14.9	13.9
	22 (CHE)	−7.6		−8.7	−6.9	−7.9	−10.9
13 + SO_2	**TS5** (*D.-A.*)	8.4		12.7	12.9	13.9	13.4
	14 (*D.-A.*)	−12.2		−8.4	−4.9	−3.1	−5.1
	TS6 (CHE)	14.4		16.2	16.3	16.4	15.9
	15 (CHE)	−10.6		−11.0	−9.7	−10.9	−13.8

[a]) From [39]. [b]) The B3LYP/6-31G(d) geometries were used for **16** and **13**.

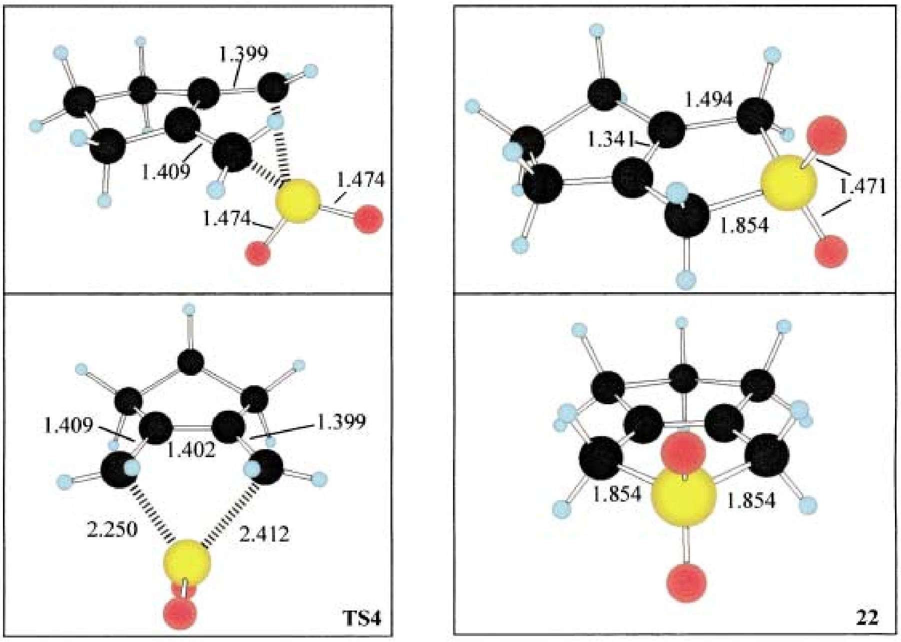


Fig. 9. *B3LYP/6-31G(d) transition structure* **TS4** *and sulfolene* **22** *corresponding to the cheletropic reaction of 1,2-dimethylidenecyclopentane* (**16**) *and* SO_2

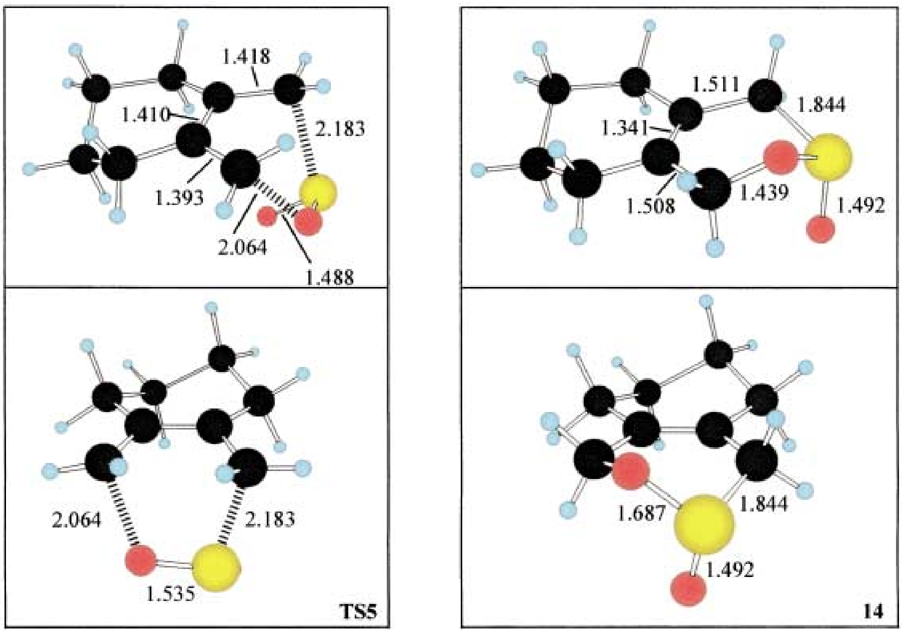


Fig. 10. *B3LYP/6-31G(d) transition structure* **TS5** *and sultine* **14** *corresponding to the hetero*-Diels-Alder *reaction of 1,2-dimethylidenecyclohexane* (**13**) *and* SO_2

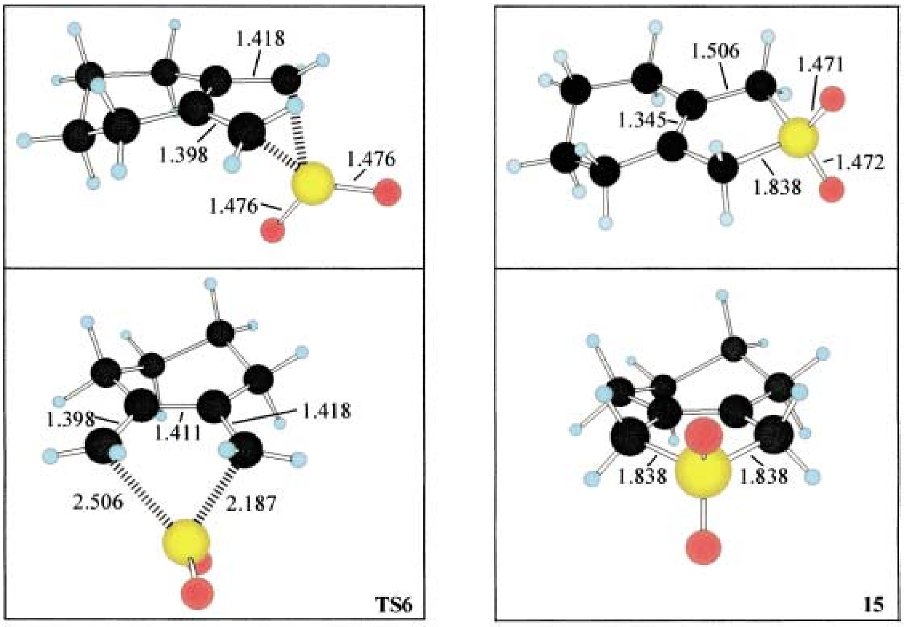


Fig. 11. *B3LYP/6-31G(d) transition structure* **TS6** *and sulfolene* **15** *corresponding to the cheletropic reaction of 1,2-dimethylidenecyclohexane* (**13**) *and* SO_2

Table 5. *Changes in Enthalpy, Entropy, and* Gibbs *Free Energy* [a]) [kcal mol^{-1}] *for the Transition Structures* **TS** *and Products of the Cheletropic* (CHE) *and Hetero*-Diels-Alder (*D.-A.*) *Reactions between Buta-1,3-diene* (**27**), *1,2-Dimethylidenecyclopentane* (**16**), *or 1,2-Dimethylidenecyclohexane* (**13**) *and* SO_2 *Giving the Corresponding Sulfolenes and Sultines*

System	Structures	ΔH (theor.)	ΔH (exper.)	ΔS (theor.)	ΔS (exper.)	ΔG (theor.)	ΔG (exper.)
27 + SO_2	**TS1** (*D.-A.*)	18.8	–	– 46.8	–	28.1	–
	28 (*D.-A.*)	– 1.6	– 7 [b])	– 47.7	–	7.9	–
	TS2 (CHE)	18.7	–	– 45.1	–	27.6	–
	29 (CHE)	– 9.9	– 16.4 [c])	– 48.0	–	– 0.4	–
16 + SO_2	**TS3** (*D.-A.*)	10.9	6.6	– 46.3	– 50	20.0	16.6
	19 (*D.-A.*)	– 5.7	– 9.0	– 45.6	– 41	3.3	– 0.9
	TS4 (CHE)	13.2	8.7	– 42.3	– 47	21.6	17.9
	22 (CHE)	– 11.8	– 19.4 [d])	– 44.3	–	– 3.0	–
13 + SO_2	**TS5** (*D.-A.*)	12.6	7.2	– 44.7	– 49	21.5	16.8
	14 (*D.-A.*)	– 6.0	– 8.9	– 45.1	– 36	3.0	– 1.4
	TS6 (CHE)	15.2	11.5 [d])	– 42.2	– 38 [d])	23.6	–
	15 (CHE)	– 14.7	– 19.4 [d])	– 44.4	–	– 5.9	–

[a]) The theoretical estimates of the thermodynamics functions were performed with G2 absolute energies (without zero-point-energy contributions) and MP2/6-31G(d) (**27**) or B3LYP/6-31G(d) (**16**, **13**) frequencies (*T* 198 K, *p* 1 atm). Unless otherwise indicated, the experimental values are those of this work (*T* 198 K). [b]) Estimation by comparison with isoprene + SO_2 [11]. [c]) [19]. [d]) [22]; at 300 K.

in contradiction with experimental evidence that shows the thermodynamic product of the **27** + SO_2 reaction to be the sulfolene **29** [2][3]. As mentioned above, this is a consequence of the lack of an appropriate number of polarization functions in the basis set employed. Indeed, the B3LYP/6-31 + G(2df,p) and B3LYP/6-311 + G(3df,2pd) energies collected in *Table 4* show sulfolene **29** to be more stable than the corresponding sultine **28**, in agreement with both G2(MP2,SVP) calculations [39] and experimental observations for the reactions of SO_2 with a large number of 1,3-dienes (this work and [11][16][18][39]). It should be stressed that, according to the data in *Table 4*, the presence of one diffuse function, two d and one f polarization functions on the heavy atoms (specially on the S-atom) and one p polarization function on the H-atoms, is enough to reproduce the experimental trends. As noted in previous works [39], the G2(MP2,SVP) level, where corrections for higher polarization functions are included [37][38], provides thermodynamic information in semiquantitative agreement with the experimental data; see ΔH, ΔS, and ΔG values in *Table 5*. Therefore, a plausible recipe to study the reactions of SO_2 with large dienes could be the following: *B3LYP/6-31G(d) geometry optimizations followed by B3LYP/6-31G + G(2df,p) single-point calculations or G2(MP2,SVP) estimates* (on the B3LYP/6-31G(d) geometries) *in order to improve the energetics.*

We now compare the calculated values (*Table 4*) obtained by our recipe for the hetero-*Diels-Alder* additions **16** + $SO_2 \rightleftharpoons$ **19** and **13** + $SO_2 \rightleftharpoons$ **14** and for the cheletropic additions **16** + $SO_2 \rightleftharpoons$ **22** and **13** + $SO_2 \rightleftharpoons$ **15**. The B3LYP/6-31G(d) optimizations lead to similar geometries for sultines **19** and **14** and sulfolenes **22** and **15** compared with the fully optimized geometries of **28** and **29**, respectively. The calculated transition structures **TS3** and **TS5** for the hetero-*Diels-Alder* additions **16** + $SO_2 \rightarrow$ **19** and **13** + $SO_2 \rightarrow$ **14**, respectively, differ only slightly from the geometry calculated for **TS1**, the transition state of the hetero-*Diels-Alder* addition **27** + $SO_2 \rightarrow$ **28**. The DFT calculations suggest that the hetero-*Diels-Alder* additions proceed through a slightly asynchronous approach (the DFT *Pauling* bond orders [42] are (0.16,0.27), (0.15,0.36), (0.12, 0.32) for the two forming bonds (CO,CS) in the **27** + $SO_2 \rightarrow$ **28**, **16** + $SO_2 \rightarrow$ **19**, and **13** + $SO_2 \rightarrow$ **14** reactions, resp.). On the other hand, the MP2 method suggests a quite synchronous mechanism for the **27** + $SO_2 \rightarrow$ **28** reaction (MP2 *Pauling* bond order [42] (0.24,0.22) for (CO,CS)). In contrast, the cheletropic additions **16** + $SO_2 \rightarrow$ **TS4** $\rightarrow$ **22** and **13** + $SO_2 \rightarrow$ **TS6** $\rightarrow$ **15** are calculated to be more asynchronous than reaction **27** + $SO_2 \rightarrow$ **TS2** $\rightarrow$ **29** (the DFT *Pauling* bond orders [42] are (0.16,0.27), (0.11,0.31), and (0.19,0.19) for the two CS forming bonds in **TS4**, **TS6**, and **TS2**, resp.). The comparison of the calculated energies (*Table 4*) shows that the B3LYP/6-31G(d) evaluations for additions **16** + $SO_2 \rightarrow$ **19/22** and **13** + $SO_2 \rightarrow$ **14/15** exhibit deficiencies similar to those noted for reactions **27** + $SO_2 \rightarrow$ **28/29** and which arise from an insufficient basis set, *i.e.*, only one d set for the S-atom, which leads to inconvenient relative stabilities for sultines and sulfolenes. Calculations at the B3LYP/6-31 + G(2df,p)//B3LYP/6-31G(d) and G2(MP2,SVP) levels provide energy values, however, that are in agreement with experiment, *i.e.*, for which the sultines are less stable than their isomeric sulfolenes. In fact, the calculated (*Table 5*) enthalpy differences ΔH(**19** $\rightleftharpoons$ **22**) = -6.1 kcal mol^{-1} and ΔH(**14** $\rightleftharpoons$ **15**) = -8.7 kcal mol^{-1} are somewhat less negative than found experimentally (*ca.* -10 kcal mol^{-1}). Importantly, the recipe leads to the prediction (*Table 5*) that the hetero-*Diels-Alder* additions

16 + SO_2 → **19** and **13** + SO_2 → **14** are faster than the corresponding cheletropic additions **16** + SO_2 → **22** and **13** + SO_2 → **15**, in agreement with our experimental results ($\Delta\Delta G\ddagger \approx 1-2$ kcal mol^{-1}).

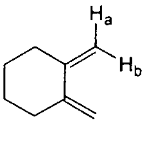
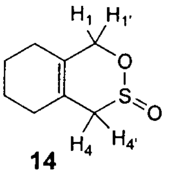
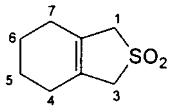
Conclusions. – Exocyclic conjugated dienes such as 1,2-dimethylidenecyclopentane (**16**), -cyclohexane (**13**), -cycloheptane (**17**), and -cyclooctane (**18**) add to sulfur dioxide giving the corresponding sultines under conditions of kinetic control ($\leq -60°$). These *Diels-Alder* reactions do not have to be promoted by a protic or *Lewis* acid. Under conditions of thermodynamic control (above $-40°$), the corresponding sulfolenes are obtained quantitavely. The heats of the hetero-*Diels-Alder* additions amount to *ca.* -9.0 kcal mol^{-1}, with entropies of reaction around -40 cal $mol^{-1}K^{-1}$, as expected for condensations in which two compounds are combined into one compound (and assuming no differential solvatation entropy between reactants and sultines!). The sulfolenes are *ca.* 10 kcal mol^{-1} more stable than their isomeric sultines, in CH_2Cl_2/SO_2 solution. The activation enthalpies for the hetero-*Diels-Alder* additions amount to *ca.* 7 kcal mol^{-1}. They are 2 kcal mol^{-1} smaller that the activation enthalpies of the corresponding cheletropic additions. Importantly, the activation entropies of the hetero-*Diels-Alder* additions ($\Delta S^{\ddagger}_1 \approx -50$ cal $mol^{-1}K^{-1}$) are significantly more negative than the corresponding reaction entropies, thus confirming that two molecules of SO_2 intervene in the transition states of the hetero-*Diels-Alder* additions of SO_2. Similar results were observed for the corresponding cheletropic additions which gave $\Delta S^{\ddagger}_2 \approx -47$ cal $mol^{-1}K^{-1}$. These results confirm predictions based on high-level *ab initio* quantum calculations carried out for the hetero-*Diels-Alder* and cheletropic additions of sulfur dioxide with butadiene [16]. Density functional theory (DFT) can be used to estimate semiquantitatively the thermodynamics and activation parameters of the SO_2 additions to large dienes provided the following recipe is applies: B3LYP/6-31G(d) geometry optimizations followed by B3LYP/6-31G + G(2df,p) single-point calculations or G2(MP2,SVP) estimates on the B3LYP/6-31G(d) geometries.

Experimental Part

General. See [43].

NMR Sample Preparation and Thermochemical Parameters. Toluene was distilled over anh. CaH_2, and SO_2 was filtered through a column of alkaline aluminium oxide *90* (act. I, *Merck*) before use. In a weighed, dry 5-mm NMR *Pyrex* tube, diene (0.05 – 0.3 mmol), toluene (internal reference, 5 – 15 mg), and CD_2Cl_2 (0.2 – 0.3 g) were mixed at 20°. The soln. was degassed by several freeze-thaw cycles at 10^{-2} Torr. Degassed SO_2 (0.1 – 0.4 ml) was transferred to the above mixture on the vacuum line. The NMR tube was sealed under vacuum. The NMR tube, frozen in liquid N_2, was defrozen at $-80°$ in liquid acetone/dry CO_2 and quickly transferred into the *Bruker ARX-400* spectrometer probe cooled to the desired temp. Other tubes were left in thermostated EtOH baths at various temp. until equilibria were reached, then transferred into the spectrometer probe cooled to the corresponding temp. When viscous solns. were obtained at temp. lower than $-70°$, mixtures of CD_2Cl_2/$CFCl_3$ were used instead of pure CD_2Cl_2. When the equilibrium-constant measurements were terminated, the NMR tube was allowed to reach r.t. and was weighed together with the piece of tube left over after sealing: this allowed verification of the exact amount of SO_2 introduced in the diene soln. Spectra were recorded for 90° pulses with delay of at least 5 T_1 of the protons of toluene (see *Table 6*), up to 180 s [44]. The equilibrium constants at a given temp. were evaluated for at least three different NMR cycloaddent ratio. Enthalpies and entropies of reactions were obtained through *Van't Hoff* plots, the equilibrium constants being determined by measuring the concentrations of the products and reactants.

Table 6. T_1 *Relaxation Times* [s] *Measured for the Proton Signals of Toluene* (internal reference), *Diene* **13**, *Sultine* **14**, *and Sulfone* **15** *at Various Temperatures and in Various Solvents* [a])

Temp. [K]	Toluene		 **13**		 **14**				 **15**		
	arom H	Me	H_a	H_b	H_1	$H_{1'}$	H_4	$H_{4'}$	$CH_2(1)$,$CH_2(3)$	$CH_2(4)$,$CH_2(7)$	$CH_2(5)$,$CH_2(6)$
198.0 [b])	7.5	3.5	2.1	2.2					0.7	0.5	0.5
203.0 [c])	9.7	4.3			0.7	0.7	0.8	0.7	1.1		
229.6 [b])	15.6	6.7	4.7	5.1					1.7	1.2	1.1
261.2 [b])	25.6	9.7	8.1	8.6					3.0	2.2	2.1
261.2 [c])	29.8	10.7							4.0	2.9	2.7
299.0 [b])	42.9	12.7	13.0	13.9					5.3	3.8	3.7

[a]) 400 MHz. [b]) In pure CD_2Cl_2. [c]) In $SO_2/CD_2Cl_2/CFCl_3$ 5 : 2 : 3.

Kinetics Measurements. NMR Tubes (5 mm) were prepared as above. ^{1}H-NMR (400 MHz) spectra were recorded for 30° pulses will delays $>3\ T_1$. When delays shorter than 3 T_1(toluene) were used, a surelevation factor was applied on the signal integrals that was measured at the end of each kinetic. This required the recording of two ^{1}H-NMR spectra of the sample, one with the same parameters as used during the kinetic, and another with 30° pulses and delay between pulses of 180 s (to ensure complete relaxation of the toluene aromatic protons used as internal reference).

1,4,5,6,7,8-Hexahydro-2,3-benzoxathiin 3-Oxide (**14**). A mixture of $CD_2Cl_2/CFCl_3$ (1% toluene) 4 : 1 (0.3 ml),SO_2 (150 mg), and **13** (40 mg, 0.37 mmol) was degassed in a 5-mm NMR tube *in vacuo* and allowed to stay at −75°. Equilibrium was reached after 8 h, giving **14**/**15** 96 : 4. Heating to −40° led to cycloreversion **14** → **13** + SO_2 and exclusive formation of **15**.

Data of **14**: ^{1}H-NMR (400 MHz, $CD_2Cl_2(CFCl_3/SO_2$, 193 K): 4.25 (*d*, ^2J = 15.9, H_b–C(1)); 4.14 (*d*, ^2J = 15.9, H_a–C(1)); 3.39 (*d*, ^2J = 17.3, H_b–C(4)); 2.75 (*d*, ^2J = 17.3, H_a–C(4)); 1.91 (*m*, $CH_2(5)$); 1.86 (*m*, $CH_2(8)$); 1.79 (*m*, $CH_2(6)$); 1.56 (*m*, $CH_2(7)$). ^{13}C-NMR (100.6 MHz, $CD_2Cl_2/CFCl_3/SO_2$, 193 K): 125.9 (*s*, C(8a)); 117.8 (*s*, C(4a)); 60.0 (*t*, ^1J(C,H) = 150, C(1)); 49.3 (*t*, ^1J(C,H) = 138, C(4)); 29.0 (*t*, ^1J(C,H) = 128, C(5)); 24.7 (*t*, ^1J(C,H) = 126, C(8)); 22.1 (*t*, ^1J(C,H) = 131, C(6)); 21.3 (*t*, ^1J(C,H) = 129, C(7)). ^{17}O-NMR (54.2 MHz, $CD_2Cl_2/CFCl_3/SO_2$, 223 K): 133 (br. *s*, O=(3); 87 (br. *s*, O(2)).

*Data of 1,3,4,5,6,7-Hexahydrobenzo[*c*]thiophene 2,2-Dioxide* (**15**): ^{1}H-NMR (400 MHz, CD_2Cl_2/SO_2, 20°): 3.68 (*m*, $CH_2(1)$, $CH_2(3)$); 2.10 (*m*, $CH_2(4)$, $CH_2(7)$); 1.78 (*m*, $CH_2(5)$, $CH_2(6)$). ^{13}C-NMR (100.6 MHz, $CD_2Cl_2SO_2$, 20°): 128.9 (*s*, C(3a), C(7a)); 60.3 (*t*, ^1J(C,H) = 142, C(1), C(3)); 26.4 (*t*, ^1J(C,H) = 127, C(4), C(7)); 22.7 (*t*, ^1J(C,H) = 129, C(5), C(6)). ^{17}O-NMR (54.2 MHz, $CDCl_3$, 25°): 160.5 ($w_{1/2}$ = 250 Hz).

*4,5,6,7-Tetrahydro-1*H*-cyclopent[*d*][1,2]oxathiin 3-Oxide* (**19**). A mixture of 1,2-dimethylidenecyclopentane (**16**) [17] (24.8 mg, 0.26 mmol), CD_2Cl_2 (310 mg), and $CFCl_3$ (239 mg) was degassed in a 5-mm NMR tube (vac. line, 10^{-2} Torr). SO_2 (554 mg, 8.65 mmol) was condensed at −196°. After melting at −78°, the tube was allowed to stay at −75° for 6.5 h, giving **19**/**22**/**16** 96.6 : 2.7 : 0.7. Above −50°, **19** isomerized to **22** quantitatively.

Data of **19**: ^{1}H-NMR (400 MHz, $CD_2Cl_2/CFCl_3/SO_2$, −60°): 4.52 (*d*, ^2J = 16.1, H_a–C(1)); 4.44 (*d*,, ^2J = 16.1, H_b–C(1)); 3.48 (*d*, ^2J = 17.0, H_a–C(4)); 3.02 (*d*, ^2J = 17.0, H_b–C(4)); 2.37–2.46 (*m*, $CH_2(5)$, $CH_2(7)$); 1.79–1.91 (*m*, $CH_2(6)$). ^{13}C-NMR (100.6 MHz, $CD_2Cl_2/CFCl_2/SO_2$, 198 K): 130.0 (*s*, C(7a)); 122.4 (*s*, C(4a)); 60.9 (*t*, ^1J(C,H) = 151, C(1)); 48.8 (*t*, ^1J(C,H) = 139, C(4)); 36.4 (*t*, ^1J(C,H) = 131, C(5)); 33.2 (*t*, ^1J(C,H) = 131, C(7)); 19.5 (*t*, ^1J(C,H) = 131, C(6)). ^{17}O-NMR (54.2 MHz, $CD_2Cl_2/CFCl_3/SO_2$, −60°): 134 (br. *s*, $w_{1/2}$ = 900 Hz, O=C(3)); 87 (br. *s*, $\nu_{1/2}$ = 1400 Hz, O(2)).

*Data of 3,4,5,6-Tetrahydro-1*H*-cyclopenta[*c*]thiophene 2,2-Dioxide* (**22**): ^{1}H-NMR (400 MHz, $CD_2Cl_2/CFCl_3/SO_2$): 3.72 (br. *t*, ^5J(1,4) = ^5J(3,6) = 1.8, CH_2 (1), $CH_2(3)$); 2.50 (*tt*, ^3J = 7.3, ^5J = 1.8, $CH_2(4)$, $CH_2(6)$); 1.78 (*quint.*, ^3J = 7.3, $CH_2(5)$). ^{13}C-NMR (100.6 MHz, $CD_2Cl_2/CFCl_3/SO_2$): 135.4 (*s*, C(3a), C(6a)); 57.9 (*t*, ^1J(C,H) =

144, C(1), C(3)); 32.4 (*t*, ${}^1J$(C,H) = 132, C(4), C(6)); 23.5 (*t*, ${}^1J$(C,H) = 131, C(5)). ^{17}O-NMR (54.2 MHz, $CD_2Cl_2/CFCl_3/SO_2$, 20°): 179.2 ($w_{1/2}$ = 175 Hz).

*4,5,6,7,8,9-Hexahydro-1*H*-cyclohept[*d*][1,2]oxathiin-3-Oxide* (**20**). A mixture of 1,2-dimethylidenecycloheptane (**17**) [17] (33.4 mg, 0.27 mmol), CD_2Cl_2 (310 mg) and $CFCl_3$ (195 mg) was degassed in a 5-mm NMR tube (vac. line, 10^{-2} Torr). SO_2 (500 mg), 7.8 mmol) was condensed at – 196°. After melting at – 78°, the tube was allowed to stand at – 75° for 15 h, giving **20/23/17** 89.3 : 3.8 : 6.9. Above – 40°, quantitative formation of **23** was observed.

Data of **20**: ^{1}H-NMR (400 MHz, $CD_2Cl_2/CFCl_3/SO_2$, – 75°): 4.33 (br. *d*, ${}^2J$ = 16.2, H_a–C(1)); 4.20 (br. *d*, ${}^2J$ = 16.2, H_b–C(1)); 3.56 (br. *d*, ${}^2J$ = 17.2, H_b–C(4)); 2.85 (br. *dd*, ${}^2J$ = 17.2, ${}^5J$(H_b–C(4), H–C(9)) = 2.2, H_b–C(4)); 2.34 – 2.28 (*m*, H_a–C(5)); 2.13 – 2.05 (*m*, H_a–C(9)); 2.06 – 1.99 (*m*, H_b–C(5)); 2.00 – 1.94 (*m*, H_b–C(9)); 1.87 – 1.80 (*m*, H_a–C(7)); 1.74 – 1.68 (*m*, H_b–C(7)); 1.63 – 1.58 (*m*, H_a–C(6), H_a–C(8)); 1.45 – 1.37 (*m*, H_b–C(6), H_b–C(8)); assignments by 2D HMQC and ^{1}H,^{1}H 2D NOESY: H_a–C(1) ↔ H_a- and H_b–C(9) (medium) H_b–C(1) ↔ H_a- and H_b–C(9) (strong) H_a–C(4) ↔ H_a–C(5) (very weak), H_a–C(4) ↔ H_b–C(5) (weak), H_b–C(4) ↔ H_a–C(5) (medium), H_b–(4) ↔ H_b–C(5) (strong), {H_a–C(5) and H_b–C(5)} ↔ {H_a–C(6) and H_b–C(6)}, H–C(9) ↔ {H_a–C(8) and H_b–C(8)}, {H_a–C(7) and H_b–C(7)} ↔ {H–C(6) and H–C(8)}. ^{13}C-NMR (100.6 MHz, $CD_2Cl_2/CFCl_3/SO_2$, – 75°): 131.2 (*s*, C(9a)); 122.7 (*s*, C(4a)); 60.7 (*t*, ${}^1J$(C,H) = 151, C(1)); 51.1 (*t*, ${}^1J$(C,H) = 138, C(4)), 35.0 (*t*, ${}^1J$(C,H) = 125, C(5)); 32.3 (*t*, ${}^1J$(C,H) = 125, C(7)); 30.3 (*t*, ${}^1J$(C,H) = 126, C(9)); 25.7 (*t*, ${}^1J$(C,H) = 126, C(6) or C(8)); 25.6 (*t*, ${}^1J$(C,H) = 126, C(8) or C(6)). ^{17}O-NMR (54.2 MHz, $CD_2Cl_2/CFCl_3/SO_2$, – 63°): 140 (br. *s*, $w_{1/2}$ = 1100 Hz, O=S(3)); 94 (br. *s*, $w_{1/2}$ = 1600 Hz, O(2)).

*3,4,5,6,7,8-Hexahydro-1*H*-cyclohepta[*c*]thiophene 2,2-Dioxide* (**23**). A mixture of **17** [17] (229 mg, 1.87 mmol), CH_2Cl_2 (0.5 ml), and SO_2 (1.2 ml, 0.8 g, 13 mmol) was degassed and allowed to stand at 20° for 14 h in a sealed tube. After opening the tube, solvent evaporation, FC (AcOEt/light petroleum ether 1 : 4) gave 326 mg (93%) of **23**. White solid. M.p. 70 – 72°. UV (MeCN): 207 (3500). IR (KBr): 2915, 2850, 1730, 1445, 1400, 1310, 1250, 1150, 1105, 835, 790, 560, 475. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.79 (*m*, CH_2(1), CH_2(3)); 2.19 (*m*, CH_2(4), CH_2(8)); 1.70 – 1.75 (*m*CH_2(6)); 1.58 – 1.63 (*m*, CH_2(5), CH_2(7)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 132.0 (*s*, C(3a), C(8a)); 61.8 (*tt*, ${}^1J$(C,H) = 142, ${}^3J$(C(1), H–C(8) = ${}^3J$(C(3), H–C(4)) = 3, C(1), C(3)); 30.2 (*t*, ${}^1J$(C,H) = 125, C(4), C(8)); 30.1 (*t*, ${}^1J$(C,H) = 125, C(6)); 25.9 (*t*, ${}^1J$(C,H) = 128, C(5), C(7)). ^{17}O-NMR (54.2 MHz, $CDCl_3$, 25°): 162.1 (br. *s*, $w_{1/2}$ = 300 Hz). CI-MS (NH_3): 204 (10, $[M + NH_4]^+$), 186 (1, $M^{+\bullet}$), 122 (28, $[M - SO_2]^{+\bullet}$), 107 (11), 76 (100). Anal. calc. for $C_9H_{14}O_2S$ (186.27): C 58.03, H 7.58, S 17.21; found: C 58.08, H 7.61, S 17.14.

*1,4,5,6,7,8,9,10-Octahydrocyclooct[*d*][1,2]oxathiin-3-Oxide* (**21**). A mixture of 1,2-dimethylidenecyclooctane (**18**) [17] (18.7 mg, 0.14 mmol), CD_2Cl_2 (380 mg), and $CFCl_3$ (156 mg) was degassed in a 5-mm NMR tube (vac. line, 10^{-2} Torr). SO_2 (145 mg, 2.3 mmol) was condensed at – 196°. After melting at – 78°, the tube was allowed to stand at – 75° for 17 h giving **21/24/18** 94 : 4.5 : 0.6 (equilibrium mixture). Heating above – 40° led to quantitative formation of **24**.

Data of **21**: ^{1}H-NMR (400 MHz, CD_2Cl_2/SO_2, – 75°): 4.39 (br. *d*, ${}^2J$ = 16.0, H_a–C(1)); 4.22 (br. *dd*, ${}^2J$ = 16.0, ${}^5J$(H_b–C(1), H–C(5)) = 1.6, H_b–C(1)); 3.49 (br. *d*, ${}^2J$ = 16.8, H_b–C(4)); 2.81 (br. *dd*, ${}^2J$ = 16.8, ${}^5J$(H_b–C(4), H–C(10)) = 1.8, H_b–C(4)); 2.30 – 2.10 (*m*, CH_2(5), CH_2(10)); 1.65 – 1.25 (*m*, CH_2(6), CH_2(7), CH_2(8), CH_2(9)). ^{13}C-NMR (100.6 MHz, $CD_2Cl_2/CFCl_3/SO_2$, – 75°): 128.6 (*s*, C(10a)); 119.3 (*s*, C(4a)); 59.9 (*t*, ${}^1J$(C,H) = 150, C(1)); 49.7 (*t*, ${}^1J$(C,H) = 137, C(4)); 30.7 (*t*, ${}^1J$(C,H) = 126, C(5)); 27.8 (*t*, ${}^1J$(C,H) = 126, C(10)); 29.0, 27.4, 26.0, 25.5 (4*t*, ${}^1J$(C,H) = 126, C(6), C(7), C(8), C(9)); assignments of C(5) and C(10) by HMQC. ^{17}O-NMR (54.2 MHz, $CD_2Cl_2/CFCl_3/SO_2$, – 68°): 136 (br. *s*, $w_{1/2}$ = 1040 Hz, O=S(3)); 87 (br. *s*, $w_{1/2}$ = 1600 Hz, O(2)).

*1,3,4,5,6,7,8,9-Octahydrocycloocta[*c*]thiophene 2,2-Dioxide* (**24**). A mixture of **18** [17] (175 mg, 1.28 mmol), CH_2Cl_2 (0.5 ml), and SO_2 (1 ml) was degassed in a *Pyrex* tube. After sealing the tube under vacuum, the mixture was allowed to stand at 20° for 14 h. Solvent evaporation and FC (AcOEt/light petroleum ether 1 : 4) gave 257 mg (100%) of **24**. White solid. M.p. 86 – 88°. UV (MeCN): 210 (3860). IR (KBr): 2910, 2860, 1470, 1400, 1305, 1245, 1125, 1105, 810, 565, 480. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.74 (*m*, CH_2(1), CH_2(3)); 2.23 (*m*, CH_2(4), CH_2(9)); 1.53 – 1.58 (*m*, CH_2(6), CH_2(7)); 1.47 – 1.51 (*m*, CH_2(5), CH_2(8)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 130.4 (*s*, C(3a), C(9a)); 59.3 (*tt*, ${}^1J$(C,H) = 142, ${}^3J$(C(1), H–C(9)) = ${}^3J$(C(3), H–C(4)) = 5, C(1), C(3)); 27.8 (*t*, ${}^1J$(C,H) = 128, C(5), C(8)); 27.1 (*t*, ${}^1J$(C,H) = 127, C(4), C(9)); 25.9 (*t*, ${}^1J$(C,H) = 127, C(6), C(7)). ^{17}O-NMR (54.2 MHz, $CD_2Cl_2/CDCl_3/SO_2$, 25°): 165.2 (br. *s*, $w_{1/2}$ = 200 Hz). CI-MS (NH_3): 218 (18, $[M + NH_4]^+$), 200 (10, $M^{+\bullet}$), 155 (11), 136 (51, $[M - SO_2]^{+\bullet}$), 121 (89), 107 (100), 98 (92), 93 (94), 79 (55). Anal. calc. for $C_{10}H_{16}O_2S$ (200.29): C 59.97, H 8.05, S 16.01; found: C 59.97, H 8.10, S 16.03.

1,2-Oxathionane-4,8-dione 2-Oxide (**25**). 1,2-Dimethylidenecyclopentane (**16**) [17] (0.2 g, 2.1 mmol) and CD_2Cl_2 (2 ml) were degassed on the vac. line. Then SO_2 (2 ml) was condensed at – 196°. The mixture was allowed to stand at – 78° for 18 h, then O_3/O_2 was bubbled through the mixture at – 78°. The yellow soln. turned orange. SO_2 was evaporated at – 78°, and an aliquot was transferred by cannula into a 5-mm NMR tube for analysis at – 20°. Above – 20°, **25** decomposed. ^{1}H-NMR (400 MHz, CD_2Cl_2, 253 K): 4.72 (*d*, $^2J = 16.4$, H_a–C(9)); 4.54 (*d*, $^2J = 16.4$, H_b–C(9)); 4.31 (*d*, $^2J = 13.7$, H_a–C(3)); 3.88 (*d*, $^2J = 13.7$, H_b–C(3)); 2.79 (*ddd*, $^2J = 11.8$, $^3J = 11.8$, $J = 3.7$, H_a–C(5) or H_a–C(7)); 2.68 (*ddd*, $^2J = 16.5$, $^3J = 6.5$, $J = 4.0$, H_a–C(7) or H_a–C(5)); 2.45 (*ddd*, $^2J = 16.5$, $^3J = 10.5$, $J = 3.7$, H_b–C(5) or H_b–C(7)); 2.27 (*ddd*, $^2J = 11.8$, $^3J = 5.9$, $J = 4.0$, H_b–C(7) or H_b–C(5)); 2.19 (*m*, H_a–C(6)); 2.01 (*m*, H_b–C(6)). ^{13}C-NMR (100.6 MHz, CD_2Cl_2, 213 K): 210.3 (*s*, C(8)); 199.8 (*s*, C(4)); 76.9 (*t*, ^1J(C,H) = 149, C(9)); 70.2 (*t*, ^1J(C,H) = 141, C(3)); 40.9 (*t*, ^1J(C,H) = 125, C(5) or C(7)); 35.9 (*t*, ^1J(C,H) = 130, C(7) or C(5)); 22.6 (*t*, ^1J(C,H) = 133, C(6)). CI-MS (NH_3): 208 (100, $[M + NH_4]^+$), 191 (30, $[M + H]^+$), 190 (75, $M^{+\bullet}$), 162 (91), 145 (49), 127 (76), 113 (38), 98 (25), 85 (61).

1-Oxa-2-thiacycloundecane-4,10-dione 2-Oxide (**26**). As described for **25**, with **17** [17] (0.2 g). ^{1}H-NMR (400 MHz, CD_2Cl_2, 219 K): 4.90 (*d*, $^2J = 14.7$, H_a–C(11)); 4.86 (*d*, $^2J = 14.3$, H_b–C(3)); 4.60 (*d*, $^2J = 14.7$, H_a–C(11)); 4.43 (*d*, $^2J = 14.3$, H_b–C(3)); 3.09 (*ddd*, $^2J = 11.8$, $^3J = 11.8$, $J = 5.0$, H_a–C(5) or H_a–C(9)); 2.91 (*dd*, $^2J = 11.5$, $^3J = 6.4$, H_a–C(9) or H_a–C(5)); 2.35 (*ddd*, $^2J = 12.7$, $^3J = 12.7$, $J = 2.2$, H_b–C(5) or H_b–C(9)); 2.21 (*ddd*, $^2J = 12.2$, $^3J = 5.1$, $J = 5.1$, H_b–C(9) or H_b–C(5)); 2.07 (*ddd*, $^2J = 12.7$, $^3J = 12.7$, $J = 12.7$, H_a–C(8) or H_a–C(6)); 1.72 – 1.82, 1.58 – 1.65, 1.44 – 1.51, 0.78 – 0.87 (4*m*, 2 H, 1 H, 1 H, 1 H, H–C(6), H–C(7), H–C(8)). ^{13}C-NMR (100.6 MHz, CD_2Cl_2, 219 K): 210.2 (*s*, C(10)); 203.1 (*s*, C(4)); 77.6 (*t*, ^1J(C,H) = 153, C(11)); 63.6 (*t*, ^1J(C,H) = 144, C(3)); 44.1 (*t*, ^1J(C,H) = 132, C(5) or C(9)); 35.3 (*t*, ^1J(C,H) = 132, C(9) or C(5)); 25.4 (*t*, ^1J(C,H) = 125, C(6) or C(8)); 24.8 (*t*, ^1J(C,H) = 130, C(8) or C(6)); 20.1 (*t*, ^1J(C,H) = 129, C(7)). CI-MS (NH_3): 236 (100, $[M + NH_4]^+$), 219 (33, $M + H]^+$), 218 (30, $M^{+\bullet}$), 190 (77, $[M - CO]^+$), 173 (34), 155 (76, $[M + H - SO_2]^+$), 123 (54), 95 (79).

We are grateful to the *Swiss National Science Foundation*, to the *Fonds Herbette* (Lausanne), and to the European *SOCRATES* (Lausanne-Oviedo) program for financial support. We thank also the *Swiss Center for Scientific Computing* (*CSCS*, Manno) for generous computing time and technical support.

REFERENCES

[1] R. B. Woodward, R. Hoffmann, in 'The Conservation of Orbital Symmetry', Academic Press, New York, 1970, p. 152.

[2] G. de Bruin, *Proc. K. Ned. Akad. Wet.* **1994**, *17*, 585; see also H. J. Backer, J. Strating, *Recl. Trav. Chim. Pays-Bas* **1934**, *53*, 525.

[3] S. D. Turk, R. L. Cobb, in '1,4-Cycloaddition Reactions', Ed. J. Hamer, Academic Press, New York, 1967, p. 13.

[4] W. L. Mock, J. J. McCausland, *Tetrahedron Lett.* **1968**, 391.

[5] O. Wichterle, J. Rocek, *Chem. Listy* **1953**, *47*, 1768; *Collect. Czech. Chem. Commun.* **1954**, *19*, 282; W. L. Mock, R. M. Nugent, *J. Am. Chem. Soc.* **1975**, *97*, 6521, 6526; see also D. C. Dittmer, M. D. Hoey, in 'The Chemistry of Sulphinic Acids, Esters and their Derivations', Ed. S. Patai, J. Wiley & Sons Ltd., New York, 1990, Chapt. 9, p. 239; S. I. Bell, M. Parvez, S. M. Weinreb, *J. Org. Chem.* **1991**, *56*, 373; L. Wald, W. Wucherpfennig, *Liebigs Ann. Chem.* **1971**, *746*, 28.

[6] B. Zwanenburg, L. Thijs, J. B. Broens, J. Strating, *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 443; P. A. T. W. Proskamp, W. V. der Liij, B. H. M. Lammerink, B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 100; P. A. T. W. Porskamp, R. C. Haltiwanger, B. Zwanenburg, *Tetrahedron Lett.* **1983**, *24*, 2035.

[7] K. Steliou, Y. Gareau, G. Milot, P. Salama, *J. Am. Chem. Soc.* **1990**, *112*, 7819; T. L. Gilchrist, J. E. Wood, *J. Chem. Soc., Perkin Trans. 1* **1992**, 9.

[8] H. Natsugari, R. R. Whittle, S. M. Weinreb, *J. Am. Chem. Soc.* **1984**, *106*, 7867 and ref. cit. therein.

[9] R. F. Heldeweg, H. Hogeveen, *J. Am. Chem. Soc.* **1976**, *98*, 2341.

[10] T. Durst, L. Téreault-Ryan, *Tetrahedron Lett.* **1978**, 2353; F. Jung, M. Molin, R. Van der Elzen, T. Durst, *J. Am. Chem. Soc.* **1974**, *96*, 935; J.-H. Liu, A.-T. Wu, M.-H. Huang, C.-W. Wu, W.-S. Chong, *J. Org. Chem.* **2000**, *65*, 3395; G. Attardo, W. Wang, J.-I. Kraus, B. Belleau, *Tetrahedron Lett.* **1994**, *35*, 4743.

[11] B. Deguin, P. Vogel, *J. Am. Chem. Soc.* **1992**, *114*, 9210.

[12] K. Alder, G. Stein, *Angew. Chem.* **1937**, *50*, 510; R. B. Woodward, T. J. Katz, *Tetrahedron* **1959**, *5*, 70; R. Hoffmann, R. B. Woodward, *Acc. Chem. Res.* **1968**, *1*, 17; J. Sauer, R. Sustmann, *Angew. Chem., Int. Ed.* **1980**, *19*, 779; D. Ginsburg, *Tetrahedron* **1983**, *39*, 2095; R. Gleiter, M. C. Böhm, *Pure Appl. Chem.* **1983**, *55*, 237; L. M. Stephenson, D. E. Smith, S. P. Current, *J. Org. Chem.* **1982**, *47*, 4170.

[13] a) J.-M. Roulet, G. Puhr, P. Vogel, *Tetrahedron Lett.* **1997**, *38*, 6201; b) B. Deguin, J.-M. Roulet, P. Vogel, *Tetrahedron Lett.* **1997**, *38*, 6197; c) S. Megevand, J. Moore, K. Schenk, P. Vogel, *Tetrahedron Lett.* **2001**, *42*, 673.

[14] V. Narkevitch, K. Schenk, P. Vogel, *Angew. Chem., Int. Ed.* **2000**, *39*, 1806.

[15] P. Vogel, in 'Advances in Theoretically Interesting Molecules', Ed. R. P. Thummel, JAI Press Inc., Greenwich, CT, 1989, Vol. 1, p. 201.

[16] T. Fernández, J. A. Sordo, F. Monnat, B. Deguin, P. Vogel, *J. Am. Chem. Soc.* **1998**, *120*, 13276.

[17] J. W. van Straten, J. J. van Norden, T. A. M. van Schaik, G. T. Franke, W. H. de Wolf, F. Bickelhaupt, *Rec. Trav. Chim. Pays-Bas* **1978**, *97*, 105; N. A. Le, J. J. Maitland, F. Bickelhaupt, W. H. de Wolf, *J. Am. Chem. Soc.* **1989**, *111*, 8491.

[18] E. Roversi, F. Monnat, K. Schenk, P. Vogel, P. Braña, J. A. Sordo, *Chem.-Eur. J.* **2000**, *6*, 1858.

[19] J. Cox, G. Pilcher, in 'Thermochemistry of Organic and Organometallic Compounds', Academic Press, London, 1970; J. B. Pedley, in 'Thermochemical Data and Structures of Organic Compounds', Thermodynamics Research Center, College Station, Texas, 1994.

[20] N. S. Isaacs, A. A. R. Laila, *J. Phys. Org. Chem.* **1994**, *7*, 178.

[21] D. Suarez, E. Iglesias, T. L. Sordo, J. A. Sordo, *J. Phys. Org. Chem.* **1996**, *9*, 17.

[22] N. S. Isaacs, A. A. R. Laila, *J. Chem. Res.* **1977**, *10*, 10.

[23] O. Dimroth, *Angew. Chem.* **1933**, *46*, 571.

[24] M. G. Evans, M. Polanyi, *Trans. Faraday Soc.* **1936**, *32*, 1340; **1938**, *34*, 11; R. P. Bell, *Proc. R. Soc. London, Ser A.* **1936**, *154*, 414.

[25] D. D. Nelson Jr., G. T. Fraser, W. Klemperer, *J. Chem. Phys.* **1985**, *83*, 945; A. Taleb-Bendiab, K. W. Hillig, II., R. L. Kuczkowski, *J. Chem. Phys.* **1991**, *94*, 6956; R. G. Bone, C. R. Le Sueur, R. D. Amos, A. D. Stone, *J. Chem. Phys.* **1992**, *96*, 8390; L. Sahriver-Mazzuoli, A. Sahriver, M. Wierzejewska-Hnat, *Chem. Phys.* **1995**, *99*, 227; R. G. A. Bone, R. F. W. Bader, *J. Phys. Chem.* **1996**, *100*, 10892; C. Groves, E. Lewars, *THEOCHEM* **2000**, *530*, 265.

[26] J. R. Grover, E. A. Walter, J. K. Newman, M. G. White, *J. Am. Chem. Soc.* **1990**, *112*, 6499; L.-W. Xu, A. Taleb-Bendiab, L.Nemes, R. L. Kuczkowski, *J. Am. Chem. Soc.* **1993**, *115*, 5723.

[27] B. Bujnicki, M. Mikołajczyl, J. Omelańczuk, in 'The Chemistry of Sulphinic Acids, Esters and their Derivatives', Ed. S. Patai, J. Wiley & Sons Ltd., 1990, Chapt. 16, p. 491.

[28] S. Braverman, in 'The Chemistry of Sulphones and Sulphoxides', Eds. S. Patai, Z. Rappoport, C. J. M. Stirling, J. Wiley, Chichester, 1988, p. 665; K. Schank, in 'Synthesis of Sulphones, Sulphoxides and Cyclic Sulphides', Ed. S. Patai, Z. Rappoport, J. Wiley, Chichester, 1994, Chapt. 1, p. 1; J. B. Baudin, S. Julia, *Bull. Soc. Chim. Fr.* **1995**, *132*, 196; D. J. Knight, G. H. Whitham, J. G. Williams, *J. Chem. Soc., Perkin Trans. 1* **1987**, 2149.

[29] O. Hinsberg, *Chem. Ber.* **1917**, *50*, 468.

[30] H. Mackle, *Tetrahedron* **1963**, *19*, 1159.

[31] R. V. Stanton, K. M. Merz Jr., *J. Chem. Phys.* **1994**, *100*, 434.

[32] E. Goldstein, B. Beno, K. N. Houk, *J. Am. Chem. Soc.* **1996**, *118*, 6036.

[33] A. D. Becke, *J. Chem. Phys.* **1992**, *97*, 9173.

[34] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[35] F. Jensen, in 'Introduction to Computational Chemistry', Wiley, Chichester, 1999.

[36] J. A. Sordo, Chem. *Phys. Lett.* **2000**, *316*, 167.

[37] L. A. Curtiss, P. C. Redfern, B. J. Smith, L. Radom, *J. Chem. Phys.* **1996**, *104*, 5148.

[38] L. A. Curtiss, K. Raghavachari, P. C. Redfern, J. A. Pople, *J. Chem. Phys.* **1997**, *106*, 1063.

[39] T. Fernández, D. Suárez, J. A. Sordo, F. Monnat, E. Roversi, A. Estrella de Castro, K. Schenk, P. Vogel, *J. Org. Chem.* **1998**, *63*, 9490.

[40] D. A. McQuarrie, in 'Statistical Thermodynamics', University Science Books, Mill Valley, CA, 1973.

[41] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millan, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelly, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, 'Gaussian 98', Gaussian Inc., Pittsburg, PA, 1998.

[42] L. Pauling, *J. Am. Chem. Soc.* **1947**, *69*, 542.
[43] K. Kraehenbuehl, S. Picasso, P. Vogel, *Helv. Chim. Acta* **1998**, *81*, 1439.
[44] D. D. Traficante, L. R. Steward, *Concepts Magn. Reson.* **1994**, *6*, 131; D. D. Traficante, *Concepts Magn. Reson.* **1992**, *4*, 153.

Received September 28, 2001