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DIELS–ALDER ADDITION OF BUTADIENE TO VARIOUS THIOCARBONYL ($R_2C{=}SO_n$, $n{=}0–2$) HETERODIENOPHILES AND *ENDO*-LONE PAIR EFFECT IN HETEROCUMULENE

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Diels–Alder reactions of various thiocarbonyl *S*-oxides and thiocarbonyl *S*,*S*-dioxides with buta-1,3-diene were studied by semiempirical AM1 and PM3 methods. Calculations show that the reactions of such unsymmetrical heterodienophiles pass through asynchronous transition states (TSs) with C=S π^* involved in the reaction. Calculated activation energies indicate that the reactivity of these heterodienophiles, viz. $R_2C=S$, $R_2C=SO$ and $R_2C=SO_2$, decrease gradually with successive addition of oxygen atoms to the thiocarbonyl sulfur. This is in good agreement with the experimental observations. The predictions based on LUMO and deformation energies show that the above reactivity trend corresponds to a gradual destabilization of LUMO of the dienophile and increase in deformation energy of both diene and dienophile with increase in the number of oxygen atoms around sulfur. Thiophosgene and their *S*-oxides in Diels–Alder reactions are found to be less reactive than the parent analogues. Monosubstituted (*Z*/*E*)-sulfines react with buta-1,3-diene to form *cis* and *trans* products through closely lying TSs. Calculations predict that (*E*)-sulfine has a higher reactivity than the *Z*-isomer, in reasonable agreement with experimental results. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

Thiocarbonyl *S*-monoxides ($R_2C=SO$) and thiocarbonyl *S*,*S*-dioxides ($R_2C=SO_2$), also referred to as sulfines and sulfenes respectively, belong to the category of heterocumulenes[1] and are known to undergo efficiently Diels–Alder cycloaddition with various dienes to form thiacyclic/thiabicyclic products.[2–6] These sulfur-centered heterocumulenes are labile and therefore have to be generated *in situ* and entrapped by further reactions.[2–5] Diels–Alder cycloadditions of sulfines and sulfenes have been the subject of several investigations; most of them experimental. Although extensive theoretical investigations have been performed on all-carbon Diels–Alder[7–9] and hetero-Diels–Alder[10–12] reactions, there have been no such mechanistic studies on the reactions of sulfines and sulfenes. Recently, we have investigated theoretically[13] the Diels–Alder addition of simple mono- and disubstituted sulfines and sulfenes with cyclopentadiene and anthracene. Earlier reports[2–6] show that these thiocarbonyls are efficient dienophiles undergoing Diels–Alder cycloaddition with reaction occurring preferentially at the C–S π bond. We have shown that the above reactions[13] are LUMO dienophile controlled and the LUMO in each of these sulfines and sulfenes is the C=S π^* orbital.

Another interesting aspect of these reactions is that the stereochemical relationship in the sulfine is predominantly retained in the cycloadduct. This can be observed if differently substituted *Z*- and *E*-isomers of sulfines or monosubstituted sulfines are reacted with dienes.[2–6] Monosubstituted sulfines are thermally highly unstable and therefore are much less investigated.[4, 5] Earlier theoretical studies[14] on sulfines and sulfenes indicate that these heterocumulenes have good configurational stability and are chemically reactive in cycloadditions. Although cycloadditions of sulfines and sulfenes are interesting and important, from both synthetic and mechanistic points of view, a detailed study on the mechanisms of these reactions is lacking, apart from our recent communication.[13] The reactions of substituted butadienes with these thiocarbonyls are both synthetically and stereochemically different from the reactions with other dienes. We therefore aimed to investigate the mechanism of Diels–Alder cycloaddition of simple and chloro-substituted sulfines and sulfenes with buta-1,3-diene through a transition state search by using AM1 and PM3 models. Reactions of parent thiocarbonyls with butadiene were also studied with a view to observing the relative reactivity of various carbon–sulfur double-

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bonded systems $>$C=S, $>$C=SO and $>$C=SO_2. Further, the relative reactivity of *Z*- and *E*-isomers of methyl and trifluoromethyl sulfines in the Diels–Alder cycloadditions with buta-1,3-diene and the stereoselectivity in the adduct formation were investigated to examine the effect on the reaction of the *endo*-lone pair on the sulfur atom.

COMPUTATIONAL DETAILS

AM1 and PM3 computations[15] were performed using the semiempirical molecular orbital package MOPAC 6·0[16] implemented on a MICROVAX II computer and using the INSIGHT II suite of programs implemented on a Silicon Graphics IRIS workstation. *Ab initio* computations were performed using Gaussian 94W[17] customized in a Pentium computer. All equilibrium and transition state (TS) structures were optimized using Baker's eigenvector following (EF) routine[18] as the convergence was faster and the results were of better quality than with other algorithms. The nature of the stationary points on the potential energy surface was characterized as minima or first-order saddle points by doing FORCE calculations. The first-order saddles were further characterized as the desired transition states by examining the eigenvectors associated with the single negative eigenvalue of the diagonalized Hessian. *Ab initio* LUMO energies and charges were obtained at the HF/6–31G* level and using the RFO (rational function optimization) option available in the Berny algorithm. Deformation energies of the diene and dienophile at the TS[9b, 19] were calculated as the energy change when the diene or dienophile distorts from the equilibrium structure to the structure in the TS.

Generally, in the Diels–Alder reaction, three π bonds undergo cleavage and one π and two σ bonds are newly formed and the bonding changes are therefore remarkable only in these bonds compared with the changes in the other parts of the reactants. For this reason, the changes in these bonds alone are quantitatively followed through bond order analysis. Percentages of bond formation (BF_i) and cleavage (BC_i) at the TS are defined[19a] as follows:

$$BF_i \text{ or } BC_i = \frac{BO_i^{\mathrm{TS}} - BO_i^{\mathrm{R}}}{BO_i^{\mathrm{P}} - BO_i^{\mathrm{R}}} \times 100$$

$$BF_{\mathrm{Ave}} = 1/n_i \sum_{i}^{\text{forming bonds}} BF_i$$

$$BC_{\mathrm{Ave}} = 1/n_j \sum_{j}^{\text{cleaving bonds}} BC_j$$

$$BFC_{\mathrm{Ave}} = \frac{1}{2}\left(BF_{\mathrm{Ave}} + BC_{\mathrm{Ave}}\right)$$

From the extent of average bond formation (BF_{Ave}) and cleavage (BC_{Ave}) at the TS, one can infer the relative domination of bond-making and -breaking processes at the TS. BFC_{Ave} is another index that is indicative of the looseness or early/late nature of the TSs for these reactions.

RESULTS AND DISCUSSION

The reactions taken up for the investigation are shown in Figure 1 and are split into two sets, Type I and Type II. The Diels–Alder reactions of thioformaldehyde (TF), thioformaldehyde *S*-monooxide (TFMO), thioformaldehyde *S,S*-dioxide (TFDO), thiophosgene (TP), thiophosgene *S*-monooxide (TPMO) and thiophosgene *S,S*-dioxide (TPDO) with buta-1,3-diene are classified as Type I, and those of monosubstituted sulfines, viz. methylsulfine (MS) and trifluoromethyl sulfine (TFMS), with the same diene as Type II. Computed AM1 and PM3 TSs (B1–B8) for the Type I reactions are drawn in Figure 2 and the TSs (B9–B16) for the Type II reactions are presented in Figure 4. The bond lengths of the forming C···S and C···C donds and the breaking C$\overset{\cdots}{-}$S bond are given in Figures 2 and 4. The glide angles (θ_1 and θ_2), twist angle (ϕ) and degree of asynchronicity (α) as defined are also presented. Figure 3 shows a sketch of the barrier connecting the reactants, TS and product states that are plotted as the relative energy versus BFC_{Ave} values. The graph is representative in that only AM1 values have been taken and the graph is drawn for a limited set of reactions. The graph visually conveys the

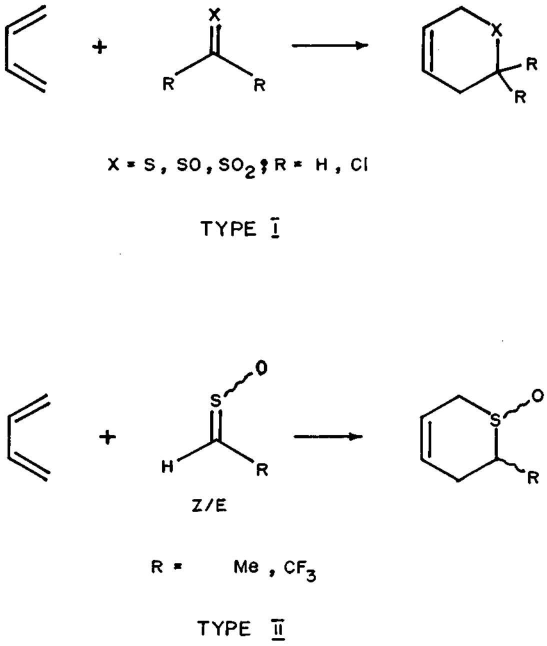
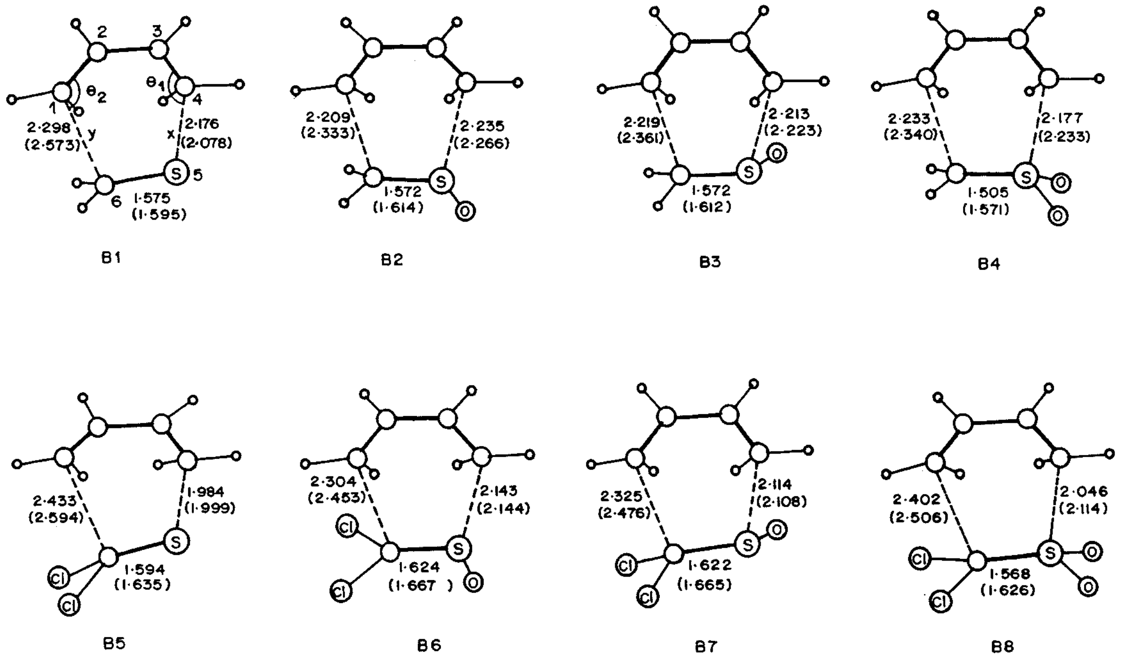


Figure 1. Scheme of various hetero-Diels–Alder reactions

relative positioning of the product and TS states for a set of closely related reactions. Table 1 gathers the AM1, PM3 and HF/6-31G* LUMO energies and the charges on C and S of these heterodienophiles. The HF/6–31G* LUMO values and charges were calculated to check the validity of the semiempirical values and this is due to an earlier report that FMO analysis based on AM1 and PM3 results are sometimes unreliable.[8b, c, 9] Calculated percentages of bond making and breaking at the TS for the Type I reactions are given in Table 2. Frontier orbital energy (FOE) gaps, quantum of charge transfer (q_{CT}), activation and reaction energies and deformation energies of both the diene and dienophile at the TS for Type I reactions are summarized in Table 3 and those for Type II reactions in Table 4.

Reactions of sulfines and sulfenes

Generally, thiocarbonyl compounds are more reactive and versatile heterodienophiles[6] than their corresponding carbonyl compounds. This is understood from the fact that thiocarbonyl bond is weaker than carbonyl bond and the longer C=S bond forces less strain during the formation of the TS.[11a] Sulfines and sulfenes are the functional derivatives of thiocarbonyls with the bent structure of the C=S=O heterocumulene bonds and are known to act as good heterodienophiles.[1–6] Hetero-Diels–Alder reactions of these thiocarbonyls were found to be concerted processes[1a, 2] and generated sulfoxide and sulfone of dihydropyran products. The FOE gaps and q_{CT} values presented in Table 3 for the



TS	θ_1 (°)	θ_2 (°)	ϕ^a (°)	α^b
B1	92·4 (96·7)	96·5 (94·4)	17·6 (19·2)	0·027 (0·016)
B2	103·9 (105·4)	97·6 (96·5)	− 12·3 (− 11·0)	0·006 (0·015)
B3	101·3 (103·4)	100·2 (98·9)	9·1 (7·6)	0·001 (0·030)
B4	107·0 (106·8)	99·3 (98·5)	− 1·0 (0·0)	0·023 (0·013)
B5	93·8 (101·4)	95·7 (95·8)	23·8 (15·7)	0·102 (0·130)
B6	107·0 (108·3)	98·5 (96·2)	− 13·4 (− 11·6)	0·036 (0·067)
B7	103·8 (106·3)	100·2 (98·8)	9·6 (8·8)	0·048 (0·080)
B8	111·2 (109·7)	98·2 (97·5)	− 1·2 (3·7)	0·080 (0·085)

[a] The torsion angle 4–5–6–1.

[b] Degree of asynchronicity as calculated from $\alpha = |x - y|/(x+y)$; x and y are the newly forming bonds.

Figure 2. AM1 (PM3) optimized TSs for the reactions of buta-1,3-diene with TF, TFMO, TFDO, TP, TPMO and TPDO

Type I reactions in Figure 1 reveal that these reactions are normal electron demand reactions and the positive q_{CT} values obtained are a clear indication of that. Some notable structural features of the TSs (B1–B8) of Type I reactions are discussed below.

Transition structure

Sulfines and sulfenes are unsymmetrical dienophiles and therefore undergo Diels–Alder reactions with buta-1,3-diene through concerted asynchronous thiacyclic TSs. The asynchronicity of the TSs is visible from the differently maturing C· · ·S and C· · ·C newly forming bonds (Figure 2) and from the calculated degree of asynchronicity (α) values noted in the same figure. The sulfur atom in thiocarbonyls is an electrophilic center and hence starts reacting first and the carbon atom is a nucleophilic center and C· · ·C formation takes place at a slower rate. This is evident from the calculated percentage of bond formation at the TS presented in Table 2 for the 4–5 and 6–1 bonds. The electrophilicity of the sulfur and nucleophilicity of the carbon atoms can be seen from the AM1 (PM3) [HF/6–31G*] charges on them listed in Table 1. The asynchronicity is more pronounced in all thiophosgene (TP, TPMO and TPDO) reactions than various thioformaldehyde (TF, TFMO and TFDO) reactions. The C–S π bond (5–6) is found to cleave 40–50% at the TS, as can be seen from the BC_i values in Table 2, and the chlorine substitution on the dienophile seems to weaken this bond to a higher degree. This is also clearly reflected in the broken C–S bond shown in Figure 2. On going from $>$C=S to $>$C=SO$_2$ heterodienophiles, the progressive addition of oxygen to the sulfur atom replaces the lone pairs on sulfur and thus the repulsion due to the lone pair on sulfur on the approaching diene is minimized. This is clearly evident from the changes in the glide angle θ_1 and the twist angle ϕ shown in Figure 2; the glide angle is found to increase while the twist angle decreases with the crowding of oxygen atoms around sulfur. Computed θ_1 and θ_2 values fall in the range 92–111°. The difference in the θ_1 and θ_2 values in the TSs (B1–B8) indicate the twisting or distortion of the diene in the TS. In TSs B2 and B6, the lone pair on sulfur is *endo* and this should lead to a larger twisting of the C_s plane. Correspondingly, when the lone pair is *exo* (TSs B3 and B7) the twisting should be lower. Calculations predict this trend well (Figure 2). The highest value of ϕ found in B1 and B5 for TF and TP reactions is due to twisting of the C_s plane to a greater degree by the repulsion of both the lone pairs on sulfur on the approaching diene. During the reaction, thiocarbonyl carbon and sulfur atoms rehybridize from sp^2 to sp^3 and this results in pyramidalization at these two sites. The extent of pyramidalization is found to be slightly greater at the sulfur site than at the carbon site.

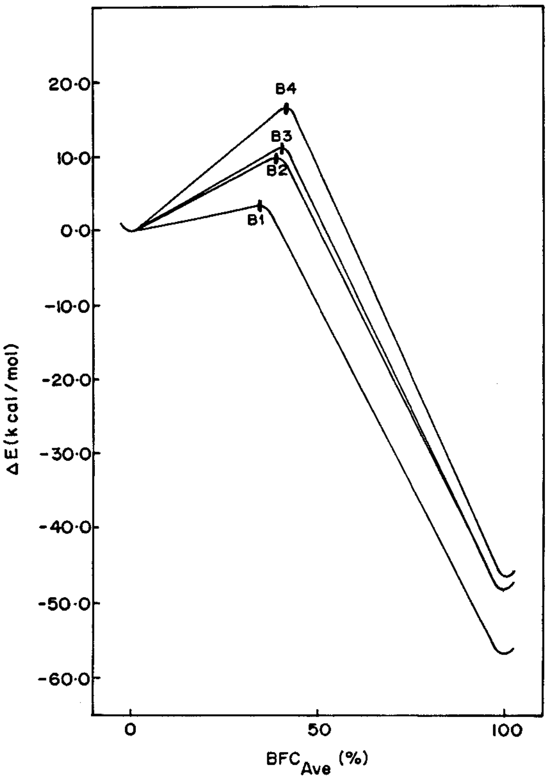
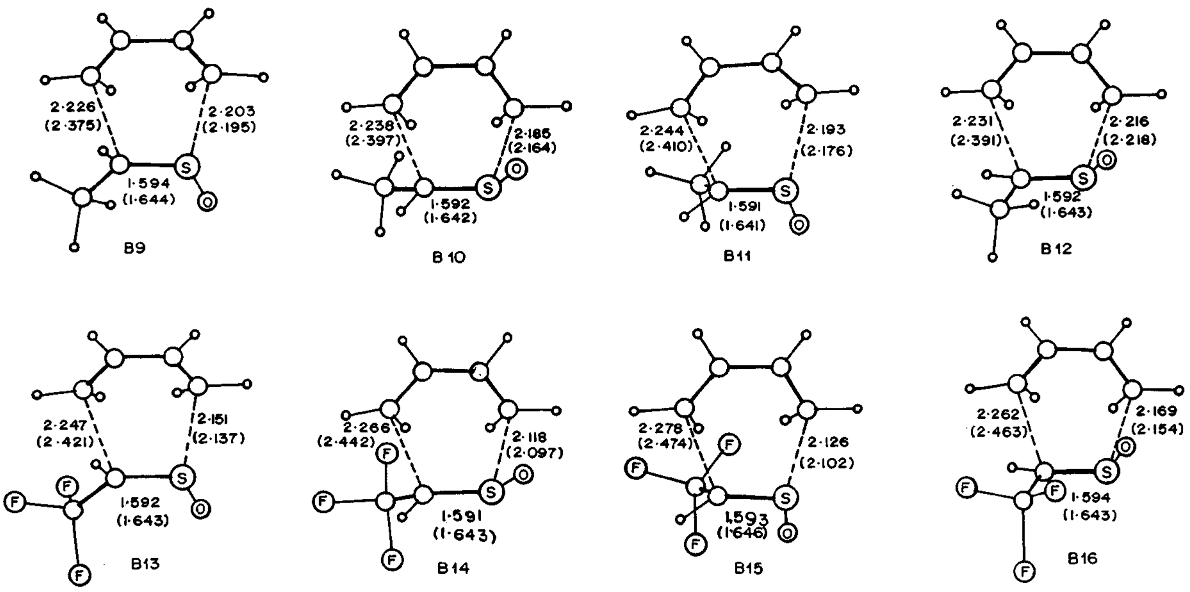


Figure 3. Plot of relative energy of TSs and products versus BFC_{Ave}; 0% and 100% of BFC$_{Ave}$ values denote reactants and products, respectively. Reactant state is taken as a reference. The representative plot is drawn based on AM1 values and for the reactions of TF, TFMO and TFDO with buta-1,3-diene.

Bond order analysis

The percentages of bond formation (BF_I) and bond cleavage (BC_i) at the TS of certain bonds calculated from bond orders are helpful in following the bonding changes during the reaction. AM1 and PM3 BFC_{Ave} values are calculated to be in the range 35–46%. Further, the BFC_{Ave} values calculated could be used to classify the TSs as either reactant-like, if the values are <50%, or product-like otherwise. BFC_{Ave} values increase in the following order: B1<B2≈B3<B4; B5<B6≈B7<B8. This indicates that the TS computed for sulfine (TFMO and TPMO) reactions occur 'earlier' than those for sulfene (TFDO and TPDO) reactions and the TS of thiocarbonyl (TF and TP) reactions occur still earlier. The degree of bonding at the TS is affected owing to the crowding of oxygen atoms on sulfur in sulfines and sulfenes. The late occurrence of the TS seem to push the barrier up and thus the expected order of reactivity of such heterodienophiles is explained. The TSs of various thiophosgene (TP, TPMO and TPDO) reactions occur slightly later than those of the corresponding parent dienophiles (TF, TFMO and TFDO), as can be seen from the BFC_{Ave} values (Table 2). The bond-cleaving processes in any reaction should normally dominate over the bond-forming processes.



TS	θ_1 (°)	θ_2 (°)	ϕ^a (°)	α^b
B9	103·8 (106·4)	99·1 (98·2)	− 7·3 (− 5·1)	0·005 (0·039)
B10	102·5 (105·2)	100·7 (98·4)	4·9 (2·4)	0·012 (0·051)
B11	101·0 (104·0)	101·3 (100·5)	13·5 (13·8)	0·011 (0·051)
B12	105·3 (107·3)	98·0 (96·0)	− 17·5 (− 17·6)	0·003 (0·038)
B13	104·9 (107·3)	98·4 (96·7)	− 5·2 (− 3·0)	0·022 (0·062)
B14	104·1 (106·3)	100·3 (97·3)	7·0 (3·9)	0·034 (0·076)
B15	102·4 (105·2)	100·4 (98·6)	16·0 (15·3)	0·035 (0·081)
B16	106·8 (108·7)	98·7 (95·0)	− 14·5 (− 15·2)	0·021 (0·070)

[a, b] See Figure 2.

Figure 4. AM1 (PM3) TS geometries for the reactions involving monosubstituted (*Z*/*E*)-sulfines (MS and TFMS) with buta-1,3-diene

Table 1. Computed AM1 (PM3) [HF/6–31G] LUMO energies (eV) and charges on C and S atoms for various thiocarbonyl heterodienophiles

Dienophile	LUMO (eV)	Charge C	Charge S
TF	− 0·821 (− 1·436) [1·540]	− 0·290 (− 0·154) [− 0·381]	0·074 (0·007) [0·056]
TFMO	− 0·422 (− 1·229) [1·796]	− 0·897 (− 1·229) [− 0·589]	1·297 (0·978) [0·795]
TFDO	0·263 (− 0·109) [2·748]	− 1·483 (− 1·121) [− 0·703]	2·835 (2·331) [1·355]
TP	− 1·686 (− 2·049) [0·680]	− 0·180 (− 0·281) [− 0·245]	0·164 (0·011) [0·047]
TPMO	− 1·305 (− 1·828) [0·871]	− 0·695 (− 0·673) [− 0·407]	1·281 (0·919) [0·857]
TPDO	− 0·693 (− 0·731) [1·905]	− 1·226 (− 1·122) [− 0·520]	2·780 (2·320) [1·419]
MS: *Z*	− 0·480 (− 1·252) [2·095]	− 0·784 (− 0·536) [− 0·383]	1·244 (0·918) [0·758]
E	− 0·503 (− 1·282) [2·041]	− 0·795 (− 0·546) [− 0·371]	1·254 (0·926) [0·753]
TFMS: *Z*	− 1·354 (− 2·126) [1·034]	− 0·944 (− 0·720) [− 0·590]	1·421 (1·094) [0·851]
E	− 1·402 (− 2·189) [0·925]	− 0·948 (− 0·721) [− 0·562]	1·427 (1·095) [0·864]

Table 2. Percentages of bond cleavage and formation at the TS for the Diels–Alder reactions of butadiene with various C=S heterodienophiles

	Bond cleavage (BC_j) at the TS			Bond formation (BF_i) at the TS					
TS	1–2	3–4	5–6	2–3	4–5	6–1	BC_{Ave}	BF_{Ave}	BFC_{Ave}
B1	32·4 (20·5)	47·8 (48·3)	39·5 (36·0)	26·5 (18·7)	38·7 (40·7)	25·3 (14·9)	39·9 (34·9)	30·2 (24·8)	35·0 (29·9)
B2	41·2 (28·3)	45·7 (37·4)	40·1 (29·9)	31·8 (22·3)	40·0 (31·2)	31·0 (20·5)	42·3 (31·9)	34·3 (24·7)	38·3 (28·3)
B3	41·4 (27·5)	48·2 (40·2)	41·7 (31·6)	32·7 (22·4)	41·4 (33·5)	31·3 (20·0)	43·8 (33·1)	35·1 (25·3)	39·5 (29·2)
B4	45·2 (32·3)	54·3 (45·2)	41·5 (33·1)	35·6 (25·6)	43·3 (35·9)	28·4 (13·1)	47·0 (36·9)	35·8 (24·9)	41·4 (30·9)
B5	33·9 (27·6)	64·9 (59·8)	50·4 (46·9)	30·3 (25·6)	57·1 (52·9)	25·0 (19·5)	49·7 (44·8)	37·5 (32·7)	43·6 (38·7)
B6	43·1 (28·9)	55·4 (47·7)	46·4 (35·3)	35·8 (24·7)	49·9 (42·5)	30·5 (19·5)	50·0 (37·3)	38·7 (28·9)	44·4 (33·1)
B7	42·5 (29·1)	57·6 (51·1)	47·1 (37·4)	36·0 (25·4)	51·5 (45·3)	29·9 (19·8)	49·1 (39·2)	39·1 (30·2)	44·1 (34·7)
B8	43·6 (31·7)	64·5 (55·5)	54·2 (39·7)	37·5 (27·3)	52·9 (46·9)	21·9 (17·2)	54·1 (42·3)	37·4 (30·5)	45·8 (36·4)

This is clearly reflected in the BC_{Ave} and BF_{Ave} values in Table 2, which are in the range 40 (32)–54 (45)% and 30 (24)–39 (33)%, respectively, for the set of the reactions investigated.

Energetics

The AM1 and PM3 activation barriers presented in Table 3 reveal that TF, TFMO, TFDO, TP, TPMO and TPDO undergo Diels–Alder reactions with buta-1,3-diene more efficiently and are faster than the butadiene–ethylene reaction. The lowest activation barrier of the butadiene–TF reaction indicates that this reaction should be much faster than the other thiocarbonyl reactions and it should be compared with a similar observation made based on MP2/6–31G* barriers[11a] obtained for butadiene–ethylene and butadiene–thioformaldehyde reactions. The reliability of the semiempirical barriers can be tested by comparing them with the experimental barriers available for a typical reaction or for a reaction of similar type, and also by correlating them with *ab initio* barriers for the same type of reactions. It is in this context that the experimental barrier reported by Zwanenburg *et al.*[2] and MP2/6–31G*[11a] and B3LYP/6–31G* barriers reported by Barone *et al.*[11c] are useful. Zwanenburg *et al.* reported that the reaction of chlorophenyl sulfine with 2,3-dimethylbuta-1,3-diene was carried out under reasonable reaction conditions and a $\Delta H^{\ddagger}$ value of 18·4 kcal mol^{-1} (1 kcal = 4·184 kJ) for this reaction was observed kinetically. A comparison of this with AM1 (PM3) barriers of sulfine (TFMO and TPMO) reactions that fall in the range 10–15 (18–21) kcal mol^{-1} (Table 3) show that PM3 seems to give reasonable barriers while the AM1 barriers are lower by a few kcal mol^{-1}. It should be noted that AM1 (PM3) activation barriers calculated for the present set of reactions are found to be in the range 3–18 (10–26) kcal mol^{-1} which are similar to the barriers obtained from MP2/6–31G* and B3LYP/6–31G* methods[11] for certain substituted thiocarbonyls (2–23 kcal mol^{-1}

Table 3. Calculated AM1 (PM3) frontier orbital energy gaps (eV), quantum of charge transfer at the TS (q_{CT}), activation and reaction energies (kcal mol^{-1}) and deformation energies of the reactants (kcal mol^{-1}) for the reactions of TF, TFMO, TFDO, TP, TPMO and TPDO and DCSE with buta-1,3-diene

Dienophile	ΔE_1[a]	ΔE_2[a]	TS	q_{CT}[b]	$\Delta E^{\neq}$	ΔE_r	DE_1[c]	DE_2[d]
Ethylene (27·5)[e]	10·8 (10·7)	11·0 (10·9)		−0·001 (0·008)	23·2 (27·0)	−58·0 (−54·0)	15·2 (14·1)	9·9 (9·2)
TF	8·5 (8·3)	9·1 (9·3)	B1	0·112 (0·119)	3·4 (9·8)	−56·6 (−59·2)	9·9 (10·0)	3·2 (1·6)
TFMO:	8·9 (8·2)	10·5 (10·3)						
exo O			B2	0·038 (0·092)	10·1 (18·3)	−47·4 (−46·9)	13·6 (10·8)	5·0 (3·2)
endo O			B3	0·042 (0·106)	11·0 (18·0)	−48·1 (−46·6)	14·2 (10·9)	5·4 (3·4)
TFDO	8·7 (9·4)	11·4 (10·4)	B4	0·007 (0·076)	16·6 (25·7)	−46·9 (−45·6)	19·2 (14·5)	12·2 (9·9)
TP	7·6 (7·4)	10·0 (9·9)	B5	0·159 (0·180)	8·6 (11·8)	−43·4 (−50·3)	15·7 (15·1)	6·5 (4·1)
TPMO:	8·0 (7·6)	10·1 (9·5)						
exo O			B6	0·098 (0·122)	14·7 (20·8)	−38·7 (−41·0)	17·4 (14·2)	8·8 (4·9)
endo O			B7	0·110 (0·145)	14·9 (19·7)	−38·3 (−41·5)	17·5 (14·4)	9·4 (5·4)
TPDO	7·7 (8·7)	10·5 (9·4)	B8	0·109 (0·154)	17·7 (25·3)	−40·4 (−42·0)	23·4 (17·5)	14·4 (12·4)

[a] $\Delta E_1 = E_{\mathrm{HOMO}}(\text{diene}) - E_{\mathrm{LUMO}}(\text{dienophile})$; $\Delta E_2 = E_{\mathrm{LUMO}}(\text{diene}) - E_{\mathrm{HOMO}}(\text{dienophile})$.

[b] Quantum of charge transfer from diene to dienophile.

[c] deformation energy of diene.

[d] deformation energy of dienophile.

[e] Experimental activation barrier (kcal mol^{-1}), from Ref. 20.

Table 4. Calculated AM1 (PM3) frontier orbital energy gaps (eV), quantum of charge transfer at the TS (q_{CT}) and activation and reaction energies (kcal mol^{-1}) for the reactions of buta-1,3-diene with MS and TFMS

Dienophile	TS	q_{CT}	$\Delta E^{\neq}$	ΔE_r
MS				
ΔE_1 (Z/E): 8·9(8·3)/8·9(8·3)				
ΔE_2 (Z/E): 10·1(10·0)/10·1(10·0)				
exo O, *exo* Me	B9	0·029 (0·079)	12·6 (20·2)	−42·1 (−42·1)
enco O, *endo* Me	B10	0·033 (0·093)	14·0 (20·0)	−41·9 (−41·4)
exo O, *endo* Me	B11	0·040 (0·106)	13·1 (20·4)	−41·2 (−41·0)
endo O, *exo* Me	B12	0·035 (0·088)	13·2 (19·7)	−42·3 (−41·0)
TFMS				
ΔE_1 (Z/E): 8·0(7·4)/8·0(7·4)				
ΔE_2(Z/E): 11·4(11·2)/11·4(10·6)				
exo O, *exo* CF_3	B13	0·912 (0·753)	11·7 (18·1)	−40·6 (−41·9)
endo O, *endo* CF_3	B14	0·924 (0·775)	13·0 (17·4)	−42·7 (−41·0)
exo O, *endo* CF_3	B15	0·941 (0·800)	11·0 (16·1)	−40·8 (−41·0)
endo O, *exo* CF_3	B16	0·914 (0·763)	12·9 (18·6)	−41·3 (−40·7)

range).

Down the series, LUMO levels (Table 1) are progressively destabilized and the quantum of charge transfer (Table 3) from diene HOMO to dienophile LUMO gradually decreases, and therefore the reactivity order expected on the basis of FMO theory is TF > TFMO > TFDO and TP > TPMO > TPDO. In full conformity with above trend, the activation barriers (Table 3) show a gradual increase from thiocarbonyl to sulfene. Experimental reports[5a] on simple sulfine and sulfene reactions suggest such a difference in reactivity. This can be clearly noted from the position of the AM1 barriers (Figure 3) of reactions of TF, TFMO and TFDO with butadiene. The barrier gradually increases and shifts to the right on going from TF to TFDO. However, a few experimental reports[5a, e, f] indicate that when substituted sulfines and sulfenes are produced in the presence of cyclopentadiene, the sulfene is trapped but sulfine is isolated unaltered. This seems to contradict earlier observations and our predictions and may perhaps be due to the effect of the substituents and the reaction conditions. One can also observe relative exothermicity of these reactions from Figure 3.

Deformation energy analysis was performed here with a view to understanding the trend in the calculated activation barriers. The deformation energies of diene (DE1) and dienophile (DE2) at the TS in Table 3 reveal that both reactants deform to different extents in their reactions. Specifically, for the set of reactions of thiocarbonyl to sulfene with butadiene, the deformation energies of both reactants increase from thiocarbonyl to sulfene. From thiocarbonyl to sulfene, the sulfur site is progressively more crowded by oxygen atoms and this has been shown to be responsible for the increased deformation of both reactants while forming the TS and hence can lead to a gradual increase in the activation barrier.

Electron-withdrawing substituents on the thiocarbonyl dienophiles are expected[2] to increase their dienophilicity and according to this thiophosgenes should be more reactive than the parent systems. The LUMO energies (Table 1) and q_{CT} values (Table 3) predict such a trend clearly. However, the computed activation barriers (Table 3) show an opposite trend; thiophosgenes (TP, TPMO and TPDO) are less reactive than simple thiocarbonyl systems (TF, TFMO and TFDO). This can happen only if the steric and electronic factors work in opposite directions and the former are overwhelmingly greater than the latter. Deformation energy analysis resolves the situation clearly. It shows that the thiophosgenes undergo a greater extent of deformation than their parent systems in the TS and this should lead to increased barriers in the former cases as opposed to the trend predicted by the FMO analysis and as one would normally expect. There is no clear experimental evidence as to which of the two—parent thiocarbonyls or their thiophosgenes—are more reactive. The reaction of TFMO and TPMO with butadiene proceeds through *exo*- and *endo*-selective TSs that can lead to axially and equatorially disposed oxygen in the respective products. The *endo* adduct is generally formed to a greater extent owing to the secondary orbital stabilization and the absence of *endo*-lone pair repulsion. In the present case, PM3 barriers correctly predict the experimental observation[5a] compared with AM1 barriers. The reaction energies calculated for title reactions show that they are exothermic and their exothermicity is comparable with the butadiene–ethylene reaction. Relatively, the reactions of various thioformaldehydes, viz. TF, TFMO and TFDO, are found to be more exothermic than those of their thiophosgene analogues.

Reactions of monosubstituted sulfines

Monosubstituted sulfines act as efficient heterodienophiles in Diels–Alder reactions and their reactions are mechanistically important as they enable one to establish the stereochemistry of the ring formation by comparing the cycloadducts of different geometrical isomers. Experimentally it has been found that the stereochemical relationship in the (*Z*/*E*)-sulfine isomers is predominantly retained in the *cis*- and *trans*-thiacyclohexene *S*-oxide adduct formation. Here, we investigated the reactions of MS and TFMS with buta-1,3-diene (Type II) and obtained four TSs and products for the reactions of *Z*/*E*-isomers. The experimental enthalpy of activation[2] has been found to be 18·4 kcal mol^{-1} for the reaction between 2,3-dimethylbuta-1,3-diene and *Z*/*E* mixtures of chlorophenyl sulfine. AM1 and PM3 barriers (Table 4) compare reasonably well with the experimental values and establish that the methods employed here are suitable for studying the present set of reactions. However, it is acknowledged that difficulties may arise owing to closely lying TSs if the analysis of various stereoselective products is performed.

The FOE gaps and q_{CT} values presented in Table 4 indicate that the reactions of MS and TFMS with buta-1,3-diene are normal electron demand-type Diels–Alder reactions. The TSs computed for such reactions are similar to the TSs formed during the reactions of simple and chlorinated sulfines discussed earlier. The computed LUMO energies, q_{CT} values and activation energies listed in Table 4 indicate that TFMS is more reactive than MS and this is a natural consequence of increased dienophilicity with more electron-withdrawing substituents. In TFMS, the CF_3 group stabilizes the LUMO by negative hyperconjugation and thus renders it the most reactive. The reaction energies (Table 4) show that the reaction of TFMS is thermodynamically less favorable than that of MS. Four distinct but closely lying TSs were obtained in each case when MS and TFMS were reacted with butadiene. The first two TSs, *exo* O, *exo* R (B9 and B13) and *endo* O, *endo* R (B10 and B14), shown in Figure 4 are due to the reactions of (*Z*)-sulfines that can lead to *cis*-ax O, eq R and *cis*-eq O, ax R products and the remaining two TSs, *exo* O, *endo* R and *endo* O, *exo* R (Figure 4), are due to the reactions of (*E*)-sulfines that lead to the formation of *trans*-ax O, ax R and *trans*-eq O, eq R products. In the reactions of (*Z*/*E*)-sulfines, (*E*)-sulfines are reported[5d] to be more reactive. A recent experimental observation on the [4+2] cycloadditions[5d] of (*Z*/*E*)-aryl sulfines[5d] with 2,3-dimethylbuta-1,3-diene show that the activation energy of the *E*-isomer reaction should be lower than that of the *Z*-isomer reaction. Although this observation is well predicted by LUMO energies and q_{CT} values, the barriers show an oscillating trend.

Stereoselectivity in monosubstituted sulfines can be mainly explained through two factors: (i) secondary orbital stabilization by the oxygen atom and the substituent on the thiocarbonyl carbon and (ii) repulsion by the lone pair on sulfur. During the formation of the TS, the diene approaches the sulfine and during this time the oxygen atom and the substituent R make a stabilizing interaction when they are in the *endo* position and the lone pair on sulfur makes a destabilizing interaction when it is in the *endo* position. Both effects are absent when these groups are in the *exo* position. The above effects act in different combinations in the four TSs and they lead to stereoselectivity.

This qualitative picture can only indicate the direction in which these effects contribute and quantitative estimates of them are difficult to make and change from case to case. Therefore, the preference can be discussed in a general context and only qualitatively. This being the case with the qualitative arguments, quantitative estimates of them through the barriers suffer from another difficulty, that is, the barriers are closely lying and therefore are difficult to resolve. Nevertheless, an attempt is made here to observe the trend in stereoselectivity in the reactions of (*Z*/*E*)-sulfines. The TSs B10 and B14 are stabilized by secondary orbital stabilization while B9 and B13 are destabilized by *endo*-lone pair repulsion. Therefore, it is straightforward that the product formation through the former TSs should be faster than that through the latter TSs. PM3 barriers support this but AM1 barriers fail to predict this. In the second set of TSs, B12 and B16, secondary orbital stabilization by the oxygen atom is present and there is no *endo*-lone pair repulsion. TSs B11 and B15 have secondary orbital interactions due to the substituent on the carbon and also *endo*-lone pair repulsion. These combinations in the above TSs predict that the former set is stabilized compared with the latter set and therefore is relatively preferred. Computed barriers could not resolve the stereoselectivity for obvious reasons and, except for this, their overall performance is reliably good.

CONCLUSIONS

Sulfines (TFMO and TPMO) and sulfenes (TFDO and TPDO) undergo Diels–Alder cycloadditions with buta-1,3-diene to form thiacyclohexene adducts. AM1 and PM3 calculations show that these reactions are LUMO dienophile controlled with C=S π bonds involved in the reaction. Sulfines and sulfenes are unsymmetrical heterodienophiles and therefore form asynchronous TSs; the sulfur atom of the dienophile, being more electrophilic, starts to react first, followed by the carbon atom. A high degree of stereochemical retention has been observed in the reactions of sulfines. Of sulfine and sulfene the former is more reactive, but both of them react less readily than thioformaldehyde. Computations show that progressive addition of oxygen atoms to sulfur gradually destabilizes the LUMO and increases the deformation energies of both the reactants at the TS. This led to a gradual increase in the barrier from $>C=S$ to $>C=SO_2$ dienophiles. The reactivity predicted here is in good agreement with the experimental results. The substitution of the chlorine atom on the thiocarbonyl carbon atom marginally increases the barrier instead of an anticipated decrease. Calculations show that chlorine atoms stabilize the LUMO on the one hand and increase the deformation energy of the reactants on the other, and these two mutually offsetting factors may be responsible for the increase in the barrier. (*Z*/*E*)-methyl and -trifluoromethyl sulfines react with buta-1,3-diene to give four distinct products. As expected, the (*E*)-sulfine is found to be more reactive than the (*Z*)-sulfine. The stereoselective preferences in these reactions are controlled by the secondary orbital stabilization by the oxygen on sulfur and the substituent on the thiocarbonyl carbon and by the *endo*-lone pair repulsion. Among these, the *endo* O, *endo* R TS turns out to be the most favorable.

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