The dimerisation of 2-methoxycarbonylbuta-1,3-diene: the importance of paralocalisation energy in assessing diene reactivity

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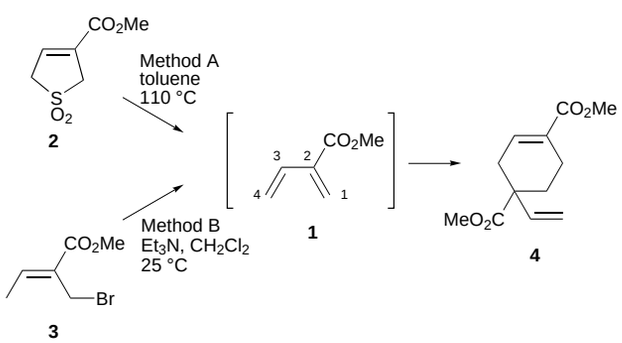
The dimerisation and competitive cycloaddition of 2-methoxycarbonylbuta-1,3-diene with electron-rich dienes has been investigated. Experimental results provide evidence that the enthalpy of the π-system significantly influences the energy of the transition state of cycloadditions of this type. This has been corroborated by *ab initio* calculations. We propose an early reorganisation of the π-electrons in such cycloadditions to explain the influence stated above.

Introduction

The facile dimerisation of 2-methoxycarbonylbuta-1,3-diene (2-MCBD) **1** to give dimethyl mikanecate **4** has been known for some time (Scheme 1).[1–6] Although the unusual ease with which



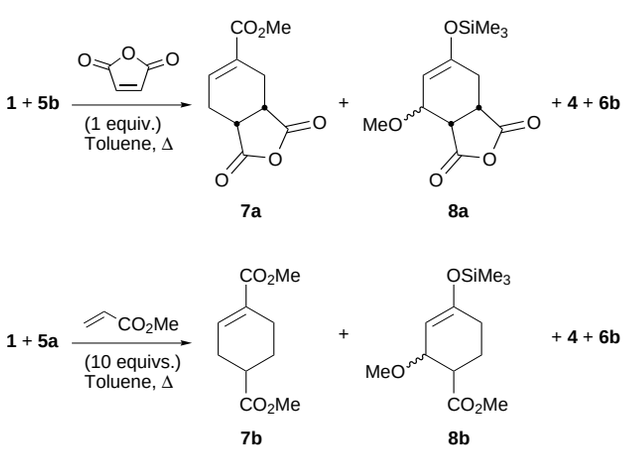
Scheme 1

this [4 + 2]-cycloaddition takes place has been noted, a rationalisation of this phenomenon has yet to be offered. A communication by Jung and Zimmerman provided the first kinetic data on this dimerisation.[7] They proposed that the high dienophilic character of the C1–C2 bond in **1** and an increased population of its s-*cis* conformation are major factors in accelerating this Diels–Alder reaction. We later provided evidence that 2-MCBD is also an activated diene from results obtained in its cross Diels–Alder reactions with electron-rich dienes. We then proposed an early reorganisation of the π-network to explain the activation of **1**.[8] We report herein a full account of this work which includes additional experimental results and *ab initio* calculations on the dimerisation of **1** supporting our hypothesis. We also extend our discussion of the rationale to include the concept of paralocalisation of electrons.

Results and discussion

A 96% yield of dimer **4** is obtained by heating sulfolene **2** at 110 °C (Scheme 1, method A)[1] or by treating the allylic bromide **3** with base at 25 °C (Method B).[2] However, in the presence of the electron-rich diene **5a** (Y = Me)[9] and the very reactive diene **5b** (Y = OMe), either method led to a mixture of dimer **4** and cross cycloadduct **6** (Table 1). In most cases, the dimerisation product prevailed unless a large excess of the electron-rich diene was used. A lower temperature seems to favour dimerisation over cross cycloaddition (entries 3, 4, 5 and 8). These results indicate that the dienophile **1** reacts more or as rapidly with itself, an electron-deficient diene, than with electron-rich dienes **5a** and **5b**. Note that the reactivity of diene **1** is underestimated here since diene **1** is generated slowly (3–4 h) and must be at a lower concentration relative to the competing diene. In the same vein, only dimer **4** was obtained when **1** was generated by method B in the presence of butadiene, isoprene or 1-methoxycarbonylbuta-1,3-diene (1-MCBD) as indicated in the last three entries. We also know that the ethyl ester analogue of **1** dimerised in preference to reacting with 2,3-dimethylbuta-1,3-diene but it reacted as a dienophile with excess cyclopentadiene at 25 °C in quantitative yield.[10] Overall, **1** (as a diene) seems to have a reactivity in between that of cyclopentadiene and diene **5a**.

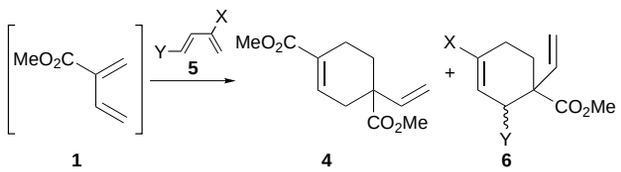
These results were puzzling in view of the fact that 2-MCBD is an electron-poor diene and we wanted to be sure that they did not arise from some artefact. Firstly, there was no evidence of hydrolysis of dienes **5** during the reaction. Secondly, we ruled out the possibility of a local concentration effect (whereby molecules of diene **1** would dimerise faster because they were generated in proximity of one another) by stirring 1 equiv. each of sulfolene **2** and diene **5b** with excess methyl acrylate (10 equiv.) in refluxing toluene (Scheme 2, bottom). After 4 h, both



Scheme 2

dienes had completely reacted to give adducts **7** and **8** respectively (GC analysis). Also detected were traces of **6b** and **4**. Much more dimer would have been detected if a proximity effect were operative. We believe that diene **1** reacted as it was generated since it or dimer **4** were not detected in significant amounts during the reaction (the extrusion of SO_2 in **2** takes *ca.* 4 h). Thirdly, an ionic mechanism is not possible for this dimerisation as suggested by the regiochemistry of dimer **4** (the other regioisomer could not be detected). To verify if a diradical mechanism were involved we repeated the dimerisation of **1**

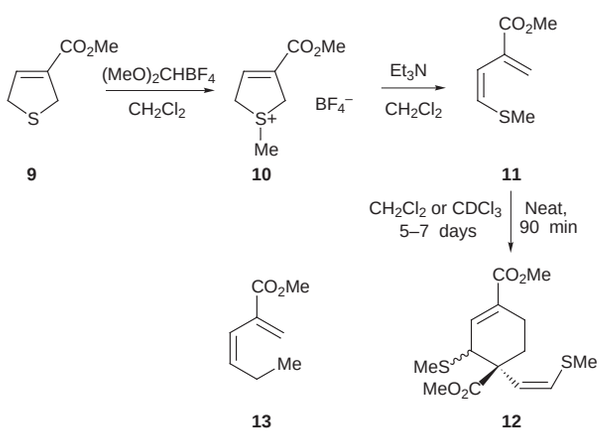
Table 1 Cross Diels–Alder reactions of diene **1**



Entry	Diene (equiv.)[a]	Y	X	Method[b]	Ratio **4**:**6**[c]	Combined yield of adducts (%)[d]
1	**5a** (1)	Me	$OSiMe_3$	A	2:1[e]	95
2	**5a** (5)	Me	$OSiMe_3$	A	1:4[e]	95
3	**5a** (1)	Me	$OSiMe_3$	B	9:1[f]	94
4	**5a** (5)	Me	$OSiMe_3$	B	3:1[f]	93
5	**5a** (>5)	Me	$OSiMe_3$	B[g]	2:1[f]	98
6	**5b** (1)	OMe	$OSiMe_3$	A	1:2[f]	89
7	**5b** (5)	OMe	$OSiMe_3$	A	1:9[f]	80
8	**5b** (1)	OMe	$OSiMe_3$	B	3:1[f]	80
9	**5c** (5)	H	H	B	1:0	95
10	**5d** (5)	H	Me	B	1:0	96
11	**5e** (5)	CO_2Me	H	B	1:0	93

[a] Molar equivalents with respect to **2** or **3**. [b] Method A: Toluene, reflux. Method B: Et_3N, CH_2Cl_2, room temp. [c] Adducts **6a** and **6b** were isolated as the hydrolysed product after chromatography on silica gel. [d] Isolated yields based on **2** or **3** after chromatography. [e] Ratios of isolated adducts. [f] Ratios determined by ^1H NMR integrations of crude mixture. [g] Slow addition of **3** over 12 h.

from **2** or **3** and its cycloaddition with methyl acrylate in the absence of light and the presence of 2,6-di-*tert*-butylphenol or hydroquinone with no effect on the rate of reaction. Yields of dimerisation are high regardless of diene concentration (including in the neat form) with no trace of [2 + 2]- or [4 + 4]-cycloaddition or polymerisation products. More convincingly, (*Z*)-2-methoxycarbonylhexa-1,3-diene **13** (see Scheme 3) does

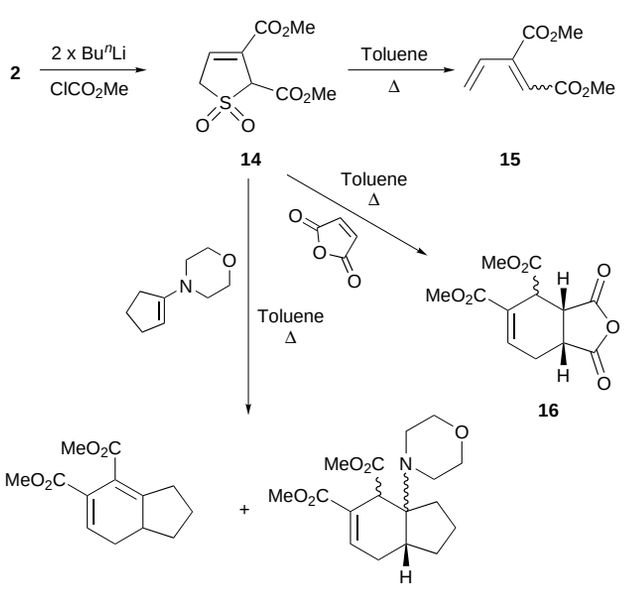


Scheme 3

not dimerise and is quite stable.[11] This compound would behave just like diene **1** if a diradical mechanism were operational but it is not expected to dimerise easily *via* a concerted cycloaddition because of the *Z*-geometry of the double bond. Therefore, the above reactions appear to proceed *via* a concerted [4 + 2]-cycloaddition mechanism.

We then attempted to make dienes **1** and **5b** compete for a separate dienophile but the results were somewhat thwarted for two reasons: on the one hand, **1** is also a powerful dienophile and will compete; on the other hand, its *in situ* generation takes time. So, when 1 equiv. of maleic anhydride was heated in toluene with equimolar amounts of **2** and **5b**, it yielded mostly dimer **4** and cycloadduct **8a** along with small amounts of adducts **7a** and **6b**. But diene **5b** alone reacted in less than 1 h with maleic anhydride at that temperature. Given the fact that the extrusion of SO_2 from **2** takes up to 4 h, it appears that the dienophile was consumed faster than **1** was generated. In addition, the reaction of **3** and **5b** with excess methyl acrylate (10 equiv.) at 25 °C following method B (3 h) gave mostly dimer **4** (73%), the expected cycloadduct **7b** (8%) and cross cycloadduct **6b** (7%), but no trace of reaction between **5b** and methyl acrylate to give **8b** (yields based on **3**). Diene **5b**, in a separate experiment, did not react at all with methyl acrylate under those conditions. Nonetheless, at that temperature **1** dimerised faster than it could add to methyl acrylate because it is a better dienophile.

Different experiments were needed to provide evidence of the activation of 2-MCBD by the ester at the 2-position. Comparison between the reactivity of 2-MCBD and some related molecules was helpful. For example, 1-methoxycarbonylbuta-1,3-diene (1-MCBD) is reluctant to dimerise and could not compete with dienes **5a** and **5b** in cycloadditions with electron-poor dienophiles. The interesting 2,3-bis(methoxycarbonyl)-buta-1,3-diene also undergoes dimerisation and reacts with electron-poor as well as electron-rich dienophiles readily.[12] We prepared dienes **11** and **15** to compare their reactivities with **1** (Schemes 3 and 4). Dihydrothiophene **9** was prepared from methyl acrylate following the method of Belleau.[13–16] After methylation with Borch's salt,[17] the resulting sulfonium salt **10**



Scheme 4

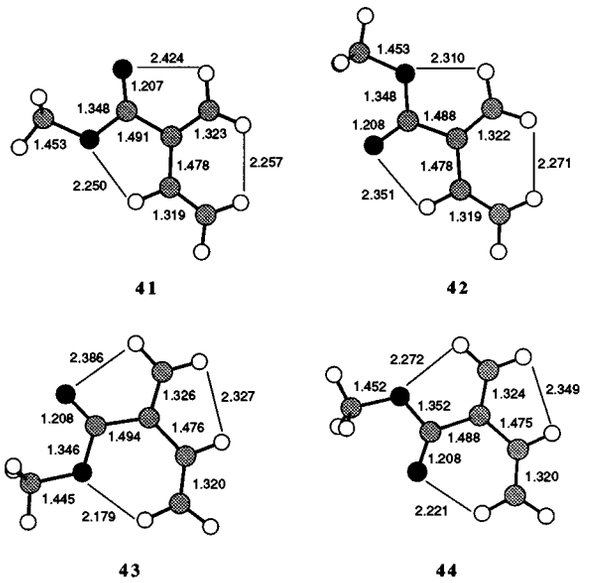


Fig. 1 RHF/3-21G optimised conformations of 2-methoxycarbonylbuta-1,3-diene

underwent an elimination reaction with triethylamine at 25 °C to yield the (*Z*)-enethiol ether **11**. Upon standing at 25 °C in a chlorinated solvent, **11** dimerised to give a 9:1 mixture of stereoisomeric adducts **12** in 5–7 days. When concentrated, **11** dimerised in 90 min in 89% yield. The ^{1}H NMR spectra of both isomers of **12** were consistent with (*Z*)-enethiol ether structures, indicative of a concerted cycloaddition mechanism. A radical or ionic mechanism would have led to isomerisation to the more stable (*E*)-enethiol ethers. The dimerisation of **11** is noteworthy because of severe steric interactions when in the cisoid conformation. Clearly the 2-methoxycarbonyl group activates **11** toward dimerisation since the known (*Z*)-1-methylthiobuta-1,3-diene does not undergo Diels–Alder reactions at all.[18] However, the sulfur also plays an activating role since the carbon analogue of **11**, (*Z*)-2-methoxycarbonylhexa-1,3-diene **13**, does not dimerise (Scheme 3).[11]

En route to diene **15**, the dianion of sulfolene **2** was acylated with methyl chloroformate to give a 78% yield of **14** (Scheme 4).[19] Upon heating in toluene for 12 h, **14** underwent a cheletropic elimination of SO_2 to afford the stable, but volatile, diene **15** as a 1:1 mixture of *E*- and *Z*-isomers. Heating **14** for 12 h in toluene containing maleic anhydride gave 87% of two isomeric cycloadducts **16** in a *ca.* 1:1.5 ratio, along with a small amount of unreacted (*E*)-**15**. Chromatography on silica gel of these adducts led to decomposition but the crude mixture was of sufficient purity for identification. Again, the reaction of the *E*-isomer is noteworthy. Contrary to diene **1**,[1] dienes **15** could also cycloadd with an electron-rich dienophile. Heating **14** in toluene in the presence of 1-morpholinocyclopentene gave 75% of the cycloaddition/elimination product **17** along with approximately 5% of isomeric cycloadducts **18**. The regiochemistry observed in adduct **17**, which was unambiguously established by NMR experiments, does not preclude an ionic mechanism in this case.

In the light of all of the above results, we concluded that the ester in 2-MCBD activates it toward cycloaddition and **1** is a diene truly more reactive than it should be as predicted by Frontier Molecular Orbital (FMO) theory.[20,21] Theoretical calculations on this dimerisation have not been reported before so we decided to undertake this task at the *ab initio* level.† Fig. 1

† All calculations have been carried out with the G92/DFT program (1) using the 3-21G basis set at the RHF level. Transition state and ground state structures were fully optimised with analytical gradient methods without symmetry constraints and characterised by analytical frequency calculations.

Table 2 Calculated energies of 2-methoxycarbonylbuta-1,3-diene conformations

Structure	Conformation	E_{total} [a]	E_{rel} [a]
41	s-*cis*	−379.435 308 1	0.76
42	s-*cis*	−379.436 318 8	0.13
43	s-*trans*	−379.434 337 4	2.31
44	s-*trans*	−379.437 058 8	0.00

[a] E_{total} = total energy (in atomic units); E_{rel} = energy relative to structure **44** (in kcal mol^{-1}); E_{rel} includes zero point vibrational energy (ZPE) correction.

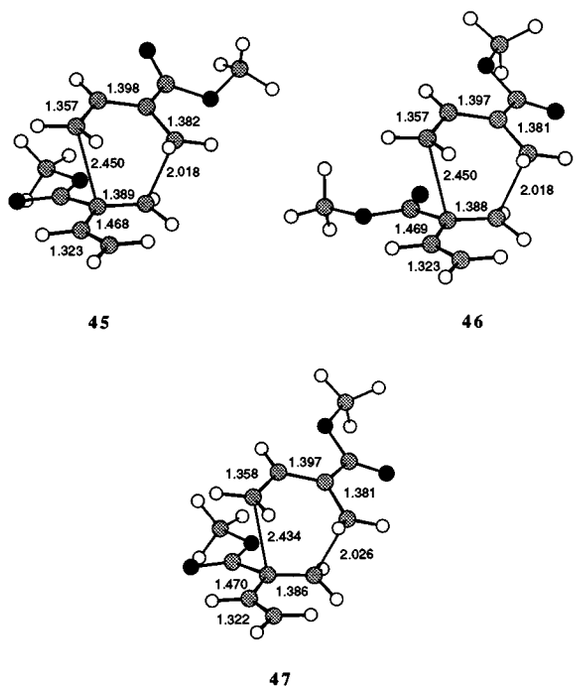
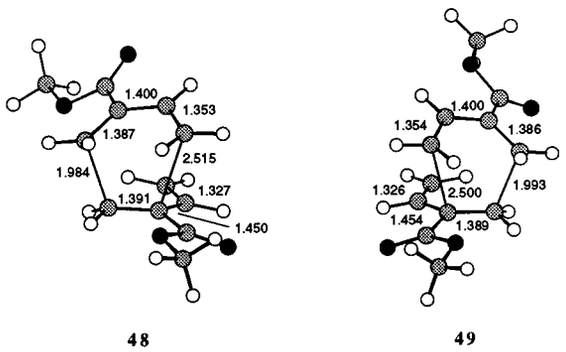


Fig. 2 RHF/3-21G optimised transition structures of the dimerisation of **1** having cisoid dienophile conformations

shows the four conformations of 2-methoxycarbonylbuta-1,3-diene that were investigated. We chose to leave the O=C–O–Me torsional angle to 0° in all structures since it is well known that this conformation is prevalent in all esters.[22,23] Therefore only the rotational preference of the carbonyl group with respect to the buta-1,3-diene system was examined. Table 2 lists the calculated energetic parameters. For the conformations of 2-methoxycarbonylbuta-1,3-diene, the lowest energy structure was the s-*trans* form **44** in which the C=O bond eclipses the C2–C3 bond of the butadiene moiety. The s-*cis* conformation **42** (C=O eclipsed with C2–C3) was only 0.13 kcal mol^{-1} higher.

Due to conformational and stereochemical issues there is a large number of possible concerted transition structures. This was one consideration for not using a higher level of theory for the calculations. In any case, geometries and bond lengths of Diels–Alder transition structures calculated at the 3-21G level are very close to those at the 6-31G level.[24] Figs. 2–4 show the ten transition structures we have examined with the activated C1=C2 double bond reacting as the dienophile. To keep the number of structures down, we have excluded other regioisomers as well as cycloadducts with the C3=C4 double bond playing the role of dienophile, all of which were not observed experimentally. One marked feature of all the transition states calculated is that they are quite asynchronous. The energetic parameters of these ten transition structures are given in Table 3. Six of the ten structures (**45**–**50**) were very similar in energy, being within 0.55 kcal mol^{-1} of each other. The other four structures (**51**–**54**) were also similar in energy, being within 2 kcal mol^{-1} of each other and within 3 kcal mol^{-1} of the former group. We calculated the dimerisation of butadiene to assess



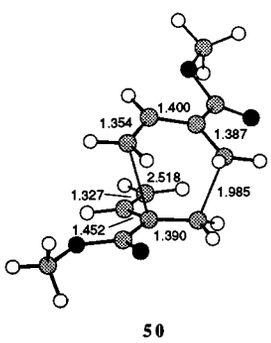
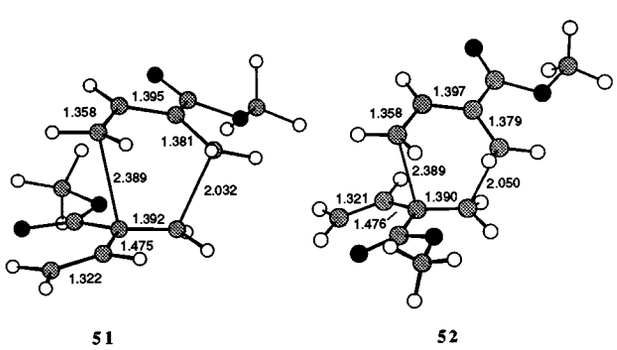


Fig. 3 RHF/3-21G optimised transition structures of the dimerisation of **1** having cisoid dienophile conformations (continued)



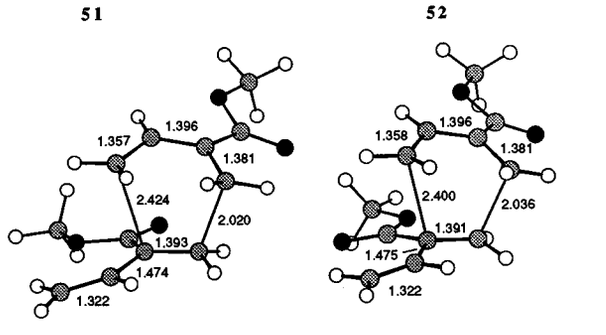


Fig. 4 RHF/3-21G optimised transition structures of the dimerisation of **1** having transoid dienophile conformations

the validity of our transition structures for 2-MCBD. Our calculations gave transition geometries very close to those calculated by Houk and the lowest calculated energy of activation was over 10 kcal mol^{-1} higher than the lowest calculated energy of activation for the dimerisation of 2-MCBD, in line with the experimental value of *ca.* 11 kcal mol^{-1}.[7,25]

The highest occupied molecular orbital (HOMO) of dienes like **1** has been shown to be of lower energy than that of buta-1,3-diene by approximately 0.2 eV, and the lowest unoccupied molecular orbital (LUMO) is lower by approximately 1 eV.[26] Our own calculations confirm these values (Table 4). When compared to buta-1,3-diene, a stronger HOMO–LUMO interaction is expected for 2-MCBD's dimerisation and this can be a factor lowering the activation barrier. However, since a lower

Table 3 Calculated energetic parameters for transition states **19**–**28**

Structure	E_{total} [a]	E_{rel} [a]	E_a [a]
45	−758.832 750	0.00	27.10
46	−758.831 738	0.35	27.98
47	−758.831 683	0.42	27.52
48	−758.832 290	0.33	27.93
49	−758.832 647	0.00	28.11
50	−758.831 681	0.53	28.17
51	−758.831 104	1.15	28.75
52	−758.829 096	2.18	29.77
53	−758.829 510	1.87	32.43
54	−758.828 012	2.83	28.77

[a] E_{total} = total energy (in atomic units); E_{rel} = energy relative to structure **45** (in kcal mol^{-1}); E_a = activation energy calculated relative to conformation **44** (in kcal mol^{-1}); E_a and E_{rel} include ZPE correction.

Table 4 Frontier molecular orbital energies of monomers [a]

Structure	HOMO	LUMO
s-*cis* butadiene	−8.85	3.59
s-*trans* butadiene	−8.85	3.36
43	−9.03	2.73
44	−9.04	2.70
41	−9.12	2.51
42	−9.14	2.50

[a] Energies are given in eV.

energy gap exists between the LUMO of **1** and the HOMO of buta-1,3-diene the cross cycloadducts should have predominated. In fact, all of the results from our cross Diels–Alder experiments cannot be reconciled with FMO arguments. The highly polarised C1=C2 bond of **1** may make it an excellent dienophile and contribute to the low activation barrier to dimerisation, but it does not explain why its cross cycloaddition with electron-rich dienes or dienophiles[1] is not favoured over dimerisation. Orbital coefficient matching should also favour the cross-cycloadditions (*e.g.* $\Sigma c^2 = 0.143$, 0.222 and 0.253 respectively for the dimerisation of **1**, its cross cycloaddition with **5b**, and its reaction with methyl vinyl ether).

Could an increased population of the cisoid conformation be responsible for the higher reactivity of 2-MCBD? Studies on the dimerisation of 2-cyanobuta-1,3-diene and its cycloaddition reactions with electron-deficient dienophiles indicate that it has a comparable reactivity to **1**.[27] Yet, 2-cyanobuta-1,3-diene does not experience a strong destabilisation of its s-*trans* conformation as 2-MCBD does.‡ In addition, the famous dimerisation of isomers **55** to Thiele's ester **56**[28] demonstrates that of the three dienes in fast equilibrium, isomer **55c** is a more reactive diene than the other two (Scheme 5).§ All of these dienes have a fixed cisoid conformation. Moreover, we have observed that the sulfolene **2** extrudes SO_2 in 3–4 h in refluxing toluene. In comparison, the unsubstituted dihydrothiophene 1,1-dioxide extrudes SO_2 four times slower at 150 °C to give butadiene. Thus, the principle of microreversibility allows us to deduce that s-*cis*-**1** reacts faster than s-*cis*-butadiene in a concerted reaction with SO_2.[20] This cheletropic addition is very much akin to the Diels–Alder reaction. All of this strongly suggests that dienes like **1** owe their enophilicity to a factor other than an enhanced population of the s-*cis* conformation.

The paralocalisation energy ($P_{1,4}$) of dienes as described by Brown and the $P_{1,2}$ energy of dienophiles represent more or less

‡ Molecular mechanics calculations using CSCChem 3D Pro™ software gives a 1.2, 1.3 and 2.3 kcal mol^{-1} preference to the s-*trans* conformations of 2-cyanobuta-1,3-diene, isoprene and buta-1,3-diene, respectively.

§ Isomers **55a** and **55c** are at low concentration, but according to the Curtin–Hammett principle **55c** must lead to the lowest-energy transition structure.

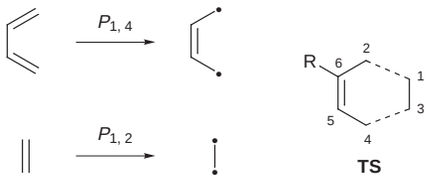
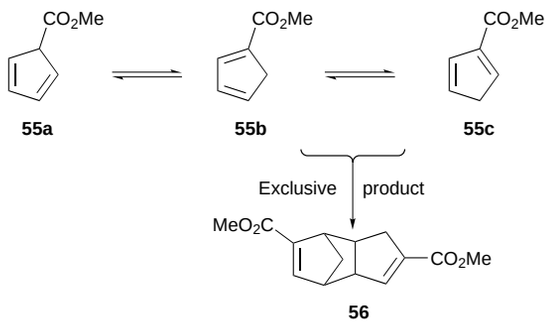


Fig. 5 Paralocalisation energy and our proposed transition state for the Diels–Alder cycloaddition

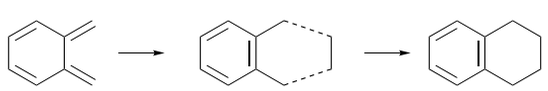


Scheme 5

the energy needed to reorganise the π-bonds in the reaction (Fig. 5).[29,30] Energetically, it represents the portion of the overall enthalpy of cycloaddition brought about by the cleavage and formation of the π-bonds only. While it is certain that some of this energy is spent on the way to the transition state for any pair of diene/dienophile, historically paralocalisation energy alone failed to predict the reactivity of most common dienes. The FMO theory proved far superior in such predictions.[20] Perhaps this is why the paralocalisation energy factor was largely ignored outside of Brown's systems, although Kiselev and Konovalov reported in 1989 that FMO and paralocalisation energies taken together did explain the order of reactivity of certain substituted anthracenes that did not follow the order predicted by the frontier orbital theory alone.[31] During cycloaddition, diene **1** goes from a cross-conjugated 6π-electron to a fully conjugated 4π-electron system and we calculated its paralocalisation energy to be 35.3 kcal mol^{-1}. Butadiene, on the other hand, goes from a conjugated 4π-electron to a non-conjugated 2π-electron array and must spend 40.5 kcal mol^{-1} as paralocalisation energy according to our calculations. The $P_{1,4}$ energy and other factors mentioned above combine to give the dimerisation of **1** the distinctly low barrier of activation of 11.12 kcal mol^{-1}.[7] One could perhaps reach the same conclusion by calculating the heat of reaction for the dimerisation of **1**. However, the latter combines π- and σ-bond energies together and is difficult to estimate qualitatively. Cyclopentadiene, in comparison, dimerises with an energy of activation of about 16 kcal mol^{-1} while the dimerisation of butadiene requires *ca*. 22 kcal mol^{-1} of activation energy.[25]

Of course, the question of exactly how much localisation energy is spent at the transition state level is not easily answered at this stage, but the sooner the π-electrons reorganise the larger the influence of $P_{1,4}$ on the TS energy. In other words, if the π-bonds have reorganised to a significant extent in the transition state and greatly precede the formation of σ-bonds, then conjugating substituents (or others) may affect the energy of the TS in ways opposite to predictions on the basis of FMO or other theories. We were therefore looking for evidence of such an early reorganisation. Our calculations revealed C5–C6 bond lengths of 1.38–1.39 Å for the dienophiles in the transition state for cycloadditions involving either butadiene or **1** (see Fig. 5 for numbering). That is a *ca.* 32% increase from their starting C5–C6 bond length of 1.32 Å. Similarly, C2–C3 bond lengths are calculated at *ca*. 1.39 Å for both dimerisations or a decrease of nearly 50% from their original length. Gratifyingly, similar bond lengths are found in a large number (if not all) of calculated Diels–Alder transition structures.[24,32,33] Hehre and Salem calculated a very short C2–C3 bond in their transition state for the reaction between buta-1,3-diene with ethylene.[32] They even suggested that 'the C1C2C3 fragment resembles its geometry in product cyclohexene far more than that in reactant butadiene'. Indeed, we propose that these changes in length are caused by an early reorganisation of π-electrons. By contrast, sigma bonds are still long at 2.0–2.4 Å for **1** and *ca*. 2.2 Å for butadiene. Bonds between C1–C2 and C3–C4 range between 1.35–1.38 Å for **1** (highly asynchronous) and *ca*. 1.36 Å for butadiene. Again, one will find close agreement between our values and those calculated by others for several Diels–Alder systems.[24,32,33] On the basis of the above discussion, we propose that the structure **TS** in Fig. 5 represents a more accurate description of the transition structure for the concerted cycloaddition than the usual one with π-electrons delocalised over the whole structure. In our TS model, there is a large double bond character between C2 and C3 which may provide further stabilisation when conjugating groups (for example) are attached to those carbons. This view of the transition structure also finds support in the theoretical treatment of ethylene–butadiene offered by Bach *et al.*[33] In their treatment, they deduced, based on geometrical and electronic standpoints, a transition state that is 'σ-early' and 'π-late' similar to that described in this paper.

In addition to the cross-cycloaddition experiments described above, other experimental observations lend support to our views. For example, the unreactive 1-MCBD has a higher paralocalisation energy and also a lower lying HOMO and LUMO, both of which will depress the reaction rate. 2,3-Bis-(methoxycarbonyl)buta-1,3-diene would be predicted to have a lower $P_{1,4}$ energy than 2-MCBD but also a lower lying HOMO and LUMO. Each will affect the reaction rate in opposite senses. Indeed, this diene dimerises at a slower rate than **1** and reacts both with electron-rich and electron-deficient dienophiles.[12] The same could be said of diene **14**. Diene **11** must have a higher lying HOMO and a low $P_{1,4}$ energy and indeed it turns out to be highly reactive despite severe steric interactions in its cisoid conformation. Compelling experimental evidence also comes from the known intense reactivity of *o*-quinodimethanes [eqn. (1)].[34,35] These dienes would develop aro-



(1)

maticity during the reaction if a transition state such as we propose is operative. Opposite to that are aryls with their high paralocalisation energy which are very unreactive dienes.

In conclusion, we submit that a lower paralocalisation energy explains the difference between the observed and expected reactivity of **1** and of its analogues. We propose that the transition structures of many Diels–Alder reactions must look like that in Fig. 5 with an early reorganisation of π-electrons. We have found support for this idea both in experiments and in theory. Admittedly, it is difficult to quantify the actual contribution of the $P_{1,4}$ energy to the transition state energy at the moment so the current analysis is largely qualitative. We are currently studying the competitive cycloaddition of other similarly activated dienes with restricted conformations in order to better isolate and quantify this phenomenon. Nevertheless, paralocalisation energies can be roughly assessed qualitatively and taking it into consideration will help predict the reactivities of starting dienes. A wider acceptance of this concept will lead, we believe, to a better prediction of diene reactivity in general.

Experimental

Unless otherwise stated all reactions were run under an atmosphere of argon using sodium–benzophenone dried solvents,

with the exception of dichloromethane which was dried using calcium hydride. Gas chromatography was conducted using a 15 m, 25μ DB-1 capillary column connected to a FID detector with electronic integration. Flash chromatography was performed by using Kieselgel 60 (230–400 mesh, Merck) silica gel. NMR spectra were recorded on a Bruker 250 or 360 MHz instrument, while infrared and mass spectra were done on a Perkin-Elmer paragon 1000 FT-IR and a Kratos Concept-H double focusing mass spectrometer, respectively. *J* Values are given in Hz.

General procedure for the cross Diels–Alder cycloadditions of diene 1 and electron-rich dienes

Method A. 3-Methoxycarbonyl-3-sulfolene **2** and the appropriate diene were heated to reflux in dry toluene for the indicated length of time. In some experiments 2,6-di-*tert*-butylphenol or hydroquinone (10 mol%) were added as radical scavengers. Then the solvent was removed *in vacuo* and the products were purified by column chromatography on silica gel eluting with the indicated solvents.

Method B. (*Z*)-1-Bromo-2-methoxycarbonylbut-2-ene **3** and the appropriate diene were dissolved in dichloromethane at 25 °C and triethylamine (3 equiv. wrt **3**) was slowly added. It was stirred at that temperature for the indicated length of time. Then the mixture was filtered through a thin pad of silica gel eluting with ethyl acetate. The solvents were removed *in vacuo* and the products were purified by chromatography as indicated.

Reaction of 3-methoxycarbonyl-3-sulfolene 2 with 2-trimethylsilyloxypenta-1,3-diene 5a

Sulfolene **2** (124 mg, 0.70 mmol) and diene **5a** were treated as described in method A for 4 h. Separation by column chromatography on silica gel eluting with hexanes–ethyl acetate (5:1) gave the dimer **4** and 4-methoxycarbonyl-3-methyl-1-trimethylsilyloxy-4-vinylcyclohexene **6a** in the indicated yield and ratio (Table 1). Product **6a** was found to be composed of a 2:1 ratio of stereoisomers as determined by integration of proton NMR signals. Adduct **6a** was characterised only by proton NMR because it was difficult to avoid partial hydrolysis of the silyl enol ether. For characterisation purposes, it was completely hydrolysed by treating it with 1 drop of conc. hydrochloric acid in a suspension of silica gel in 4 ml of ethyl acetate for 1 h followed by filtration on a pad of silica gel eluting with ethyl acetate. After evaporation of the solvent the product was purified by column chromatography on silica gel, eluting with hexanes–ethyl acetate (5:1) to yield 4-methoxycarbonyl-3-methyl-4-vinylcyclohexanone **9** as a colourless oil (65% yield). This product was also found to be a 2:1 mixture of stereoisomers by integration of proton NMR signals. For the major isomer of **6a**: δ_H(250 MHz, $CDCl_3$) 5.75 (dd, 1H, *J* 10.2, 17.8), 5.13 (dd, 1H, *J* 0.5, 10.2), 5.12 (dd, 1H, *J* 0.5, 17.8), 4.81 (br d, 1H, *J* 5.6), 3.61 (s, 3H), 2.5–1.6 (m, 5H), 0.88 (d, 3H, *J* 6.5). For the minor isomer of **6a**: δ_H(250 MHz, $CDCl_3$) 5.78 (dd, 1H, *J* 10.2, 17.0), 5.10 (dd, 1H, *J* 0.5, 10.2), 5.06 (dd, 1H, *J* 0.5, 17.0), 4.85 (dt, 1H, *J* 0.7, 5.6), 3.68 (s, 3H), 2.5–1.6 (m, 5H), 0.86 (d, 3H, *J* 6.5). For the major isomer of **9**: δ_H(250 MHz, $CDCl_3$) 5.94 (dd, 1H, *J* 10.8, 17.6), 5.32 (d, 1H, *J* 10.8), 5.28 (d, 1H, *J* 17.6), 3.64 (s, 3H), 2.5–2.0 (m, 7H), 0.92 (d, 3H, *J* 7.5); δ_C(62.9 MHz, $CDCl_3$) 210.5 (s), 173.8 (s), 139.0 (d), 116.9 (t), 52.0 (s), 51.2 (q), 44.6 (t), 38.5 (d), 37.3 (t), 27.5 (t), 16.6 (q); ν_{max}($CHCl_3$)/cm^{-1} 1720 (s), 1630 (m); *m*/*z* (CI) 237 (5%, M + 41), 225 (15, M + 29), 197 (100, M + 1), 165 (5), 137 (10) (HRMS calc. for $C_{11}H_{17}O_3$: 197.1178. Found: 197.1145). For the minor isomer of **9**: δ_H(250 MHz, $CDCl_3$) 5.82 (dd, 1H, *J* 10.8, 17.6), 5.24 (dd, 1H, *J* 0.5, 10.8), 5.13 (dd, 1H, *J* 0.5, 17.6), 3.70 (s, 3H), 2.5–2.0 (m, 7H), 0.84 (d, 3H, *J* 7.5); δ_C(62.9 MHz, $CDCl_3$) 210.4 (s), 174.5 (s), 137.9 (d), 116.8 (t), 52.0 (s), 51.2 (q), 45.7 (t), 38.0 (t), 37.0 (d), 26.9 (t), 15.4 (9).

Reaction of (*Z*)-1-bromo-2-methoxycarbonylbut-2-ene 3 with 2-trimethylsilyloxypenta-1,3-diene 5a

Bromide **3** (124 mg, 0.70 mmol) and diene **5a** were treated as described in method B. After a careful filtration on silica gel eluting with ethyl acetate the dimer **4** and adduct **6a** were obtained in the indicated yield and ratio as determined by integration of appropriate signals in their proton NMR spectra (Table 1). The adduct **6a** was found to be composed of a 3:1 ratio of stereoisomers.

Reaction of 3-methoxycarbonyl-3-sulfolene 2 with 1-methoxy-3-trimethylsilyloxybuta-1,3-diene 5b

Sulfolene **2** (176 mg, 1.0 mmol) and diene **5b** were treated as described in method A. After column chromatography on silica gel eluting with hexanes–ethyl acetate (3:1), the dimer **4** and 4-methoxycarbonyl-4-vinylcyclohex-2-enone **10** (the hydrolysis-elimination product of **6b**) were obtained in the indicated yield and ratio (Table 1). Adduct **6b** could be isolated if only a short filtration on silica gel was performed and it was found to be mostly one stereoisomer as determined by proton NMR analysis. For **6b**: δ_H(250 MHz, $CDCl_3$) 5.66 (dd, 1H, *J* 10.2, 18.0), 5.16 (d, 1H, *J* 10.2), 5.14 (d, 1H, *J* 18.0), 5.11 (d, 1H, *J* 5.9), 3.92 (d, 1H, *J* 5.9), 3.67 (s, 3H), 3.27 (s, 3H), 2.3–1.9 (m, 4H), 0.16 (s, 9H). For **10**: δ_H(250 MHz, $CDCl_3$) 6.95 (d, 1H, *J* 10.2), 6.05 (d, 1H, *J* 10.2), 5.94 (dd, 1H, *J* 10.7, 18.0), 5.27 (d, 1H, *J* 10.7), 5.13 (d, 1H, *J* 18.0), 3.72 (s, 3H), 2.5–2.0 (m, 4H); ν_{max}($CHCl_3$)/cm^{-1} 1730 (s), 1680 (s); *m*/*z* (CI) 209 (10%, M + 29), 181 (100, M + 1), 149 (13), 121 (10) (HRMS calc. for $C_{10}H_{12}O_3$: 181.0865. Found: 181.0878).

Reaction of (*Z*)-1-bromo-2-methoxycarbonylbut-2-ene 3 with 1-methoxy-3-trimethylsilyloxybuta-1,3-diene 5b

Bromide **3** (100 mg, 0.52 mmol) and diene **5b** were treated as described in method B. After a short filtration on silica gel eluting with ethyl acetate, the dimer **4** and adduct **6b** were obtained in the indicated yield and ratio as determined by proton NMR integration (Table 1). Product **6b** was found to be mostly one stereoisomer.

Competition between 3-methoxycarbonyl-3-sulfolene 2 and 1-methoxy-3-trimethylsilyloxybuta-1,3-diene 5b for methyl acrylate

3-Methoxycarbonyl-3-sulfolene **2** (100 mg, 0.57 mmol), diene **5b** (98 mg, 0.57 mmol) and methyl acrylate (488 mg, 5.7 mmol) were heated to reflux in 3 ml of toluene. The reflux was stopped after 30 min, 1 h, 2 h, 3 h, 4 h and 5 h and a GC trace of the reaction mixture was taken each time. After 4 h no more product **7** could be observed forming. After 5 h product **8** had formed in 97% yield. The solvents were removed *in vacuo* and the product directly chromatographed on silica gel using hexanes–ethyl acetate (3:1) as eluent to yield 91 mg (81%) of 1,4-bis(methoxycarbonyl)cyclohexene **7** and 73 mg (83%) of a 2.5:1 inseparable mixture of the known 4-methoxycarbonylcyclohex-2-enone and 4-methoxycarbonylcyclohex-3-enone (hydrolysis/elimination products of **8**). Adduct **7** was found to be a mixture of inseparable regioisomers by ^{13}C NMR analysis. Neither gas chromatography nor ^1H NMR spectroscopy could be used to identify these two regioisomers. A trace (<5%) of the dimer **4** accompanied adduct **7** and could be seen in both proton and carbon NMR spectra. No effort was made to separate this mixture.

The reaction was repeated with sulfolene **2** and methyl acrylate and then, separately, with diene **5b** and methyl acrylate. Each reaction was monitored by GC as above. The lengths of the reactions were the same as for the above experiment. For **7**: δ_H(250 MHz, $CDCl_3$) 6.92 (m, 1H), 3.69 (s, 3H), 3.66 (s, 3H), 2.6–1.6 (m, 7H); ν_{max}($CHCl_3$)/cm^{-1} 1730–1705 (br s), 1645 (s); *m*/*z* (CI) 239 (5%, M + 41), 227 (8, M + 29), 199 (5, M + 1), 167 (100), 139 (90) (HRMS calc. for $C_9H_{11}O_3$: 167.0708. Found: 167.0702). For the major isomer of **7**: δ_C(75.5 MHz, $CDCl_3$)

175.4 (s), 167.3 (s), 137.4 (d), 129.7 (s), 51.8 (q), 51.5 (q), 38.18 (d), 27.8 (t), 24.8 (t), 23.4 (t). For the minor isomer of **7**: δ_C(75.5 MHz, $CDCl_3$) 175.3 (s), 167.2 (s), 138.8 (d), 128.6 (s), 51.7 (q), 51.5 (q), 38.7 (d), 26.4 (t), 24.9 (t), 23.9 (t). For the major hydrolysis product of **8**: δ_H(250 MHz, $CDCl_3$) 6.95 (m, 1H), 3.72 (s, 3H), 3.00 (d, 2H, *J* 1.0), 2.75 (t, 2H, *J* 6.5), 2.5–2.4 (m, 2H); ν_{max}($CHCl_3$)/cm^{-1} 1725 (s), 1670 (br s); *m*/*z* (EI) 155 (100, M + 1). For the minor hydrolysis product of **8**: δ_H(250 MHz, $CDCl_3$) 7.05 (dd, 1H, *J* 1.0, 10.5), 6.04 (dd, 1H, *J* 1.0, 10.5), 3.72 (s, 3H), 3.40 (m, 1H), 2.6–2.1 (m, 4H).

Competition between (*Z*)-1-bromo-2-methoxycarbonylbut-2-ene 3 and 1-methoxy-3-trimethylsilyloxybuta-1,3-diene 5b for methyl acrylate

Bromide **3** (100 mg, 0.52 mmol), diene **5b** (89 mg, 0.52 mmol) and methyl acrylate (446 mg, 5.2 mmol) were dissolved in 3 ml of dichloromethane. Triethylamine was slowly added and the reaction was left to stir at 25 °C for 3 h. After filtration on a pad of silica gel eluting with ethyl acetate, the solvents were removed *in vacuo* and the product directly chromatographed on silica gel using hexanes–ethyl acetate (3 : 1) as eluent to yield 42 mg (73%) of dimer **4**, 8 mg (8%) of **7** and 7 mg (7%) of **8**.

3-Methoxycarbonyl-2,5-dihydro-1-methylthiophenium tetrafluoroborate 9

Dimethoxycarbonium tetrafluoroborate (699 mg, 4.32 mmol) was added to a solution of dihydrothiophene **2** (500 mg, 3.45 mmol) in 3 ml of dry dichloromethane. After stirring overnight at 25 °C, 5 ml of ethyl acetate were added and the mixture was stirred vigorously. When the stirring was stopped, the upper layer of solvent was carefully removed from a yellowish oil using a Pasteur pipette. Then fresh ethyl acetate (5 ml) was added and the mixture stirred vigorously for 5 min. The upper layer of solvent was removed and this process was repeated three times. Then the oily residue was put under high vacuum for 24 h leaving the slightly hygroscopic sulfonium salt **10** as a white crystalline compound. The product could be used without further purification in the next step. For characterisation purposes it could be recrystallised from hot ethyl acetate; mp 82–84 °C; δ_H(250 MHz, [$^2H_6$]DMSO) 6.93 (br s, 1H), 4.55–4.10 (m, 4H), 3.73 (s, 3H), 2.78 (s, 3H); ν_{max}(KBr)/cm^{-1} 1710 (br s), 1650 (br s), 1050 (br s); *m*/*z* 159 (7%, M^+), 158 (67), 143 (100) (HRMS calc. for $C_7H_{11}O_2S$: 159.0480. Found: 159.0440).

3-Methoxycarbonyl-1-methylthiobuta-1,3-diene 11

Triethylamine (617 mg, 6.09 mmol) was added to a suspension of sulfonium salt **10** at 25 °C. It was stirred until the mixture became homogeneous (15–30 min). The mixture was then filtered through a pad of silica gel eluting with dichloromethane taking care to keep the product in solution at all times. The diene **11** thus obtained can be characterised by NMR analysis with little dimerisation; δ_H(250 MHz, $CDCl_3$) 6.50 (s, 1H), 6.33 (s, 2H), 5.86 (s, 1H), 3.75 (s, 3H), 2.35 (s, 3H); δ_C(75.5 MHz, $CDCl_3$) 166.8 (s), 134.9 (s), 132.7 (d), 126.4 (d), 119.1 (t), 60.0 (q), 18.7 (q).

1,4-Bis(methoxycarbonyl)-3-methylthio-4-{1-methylthioethenyl}cyclohexene 12

3-Methoxycarbonyl-1-methylthiobuta-1,3-diene **33** was stirred in a dichloromethane or deuterated chloroform solution for 3 days to yield **12** as a 4 : 1 mixture of α- and β-stereoisomers. Alternatively, diene **11** was left in the neat form for 60–90 min, after which time dimerisation was complete. The product was then purified by column chromatography on silica gel eluting with hexanes–ethyl acetate (3 : 1). For the major isomer: δ_H(360 MHz, $CDCl_3$) 6.97 (dt, 1H, *J* 1.7, 5.2), 6.05 (d, 1H, *J* 10.5), 5.44 (d, 1H, *J* 10.5), 3.99 (br d, 1H, *J* 5.2), 3.62 (s, 6H), 2.4–1.7 (m, 4H), 2.18 (s, 3H), 2.12 (s, 3H); δ_C(75.5 MHz, $CDCl_3$) 173.1 (s), 166.9 (s), 137.6 (d), 130.5 (d), 127.7 (s), 127.5 (d), 52.2 (q), 51.4 (q), 50.4 (s), 46.6 (d), 27.9 (t), 21.7 (t), 17.8 (q), 17.2 (q); ν_{max}($CHCl_3$)/cm^{-1} 1730 (br s), 1650 (w), 1110 (s); *m*/*z* (EI) 316 (8%, M^+), 269 (43, −SMe), 158 (68), 140 (100) (HRMS calc. for $C_{14}H_{20}O_4S_2$: 316.0803. Found: 316.0764). For the minor isomer: δ_H(360 MHz, $CDCl_3$) 6.87 (dm, 1H, *J* 5.4), 5.94 (d, 1H, *J* 10.5), 5.15 (d, 1H, *J* 10.5), 3.99 (br d, 1H, *J* 5.2), 3.67 (s, 3H), 3.64 (s, 3H), 2.4–1.7 (m, 4H), 2.17 (s, 3H), 2.05 (s, 3H); δ_C(75.5 MHz, $CDCl_3$) 172.8 (s), 166.8 (s), 135.2 (d), 130.9 (d), 130.1 (s), 126.4 (d), 51.8 (q), 51.5 (q), 51.3 (s), 49.2 (d), 22.2 (t), 21.4 (t), 17.2 (q), 16.3 (q).

2,3-Bis(methoxycarbonyl)-3-sulfolene 14

To a stirred solution of 3-methoxycarbonyl-3-sulfolene **2** (1.6 g, 9.08 mmol) in 200 ml of dry THF at −78 °C was added 10.1 ml of Bu″Li (1.8 M in hexanes, 18.16 mmol). After stirring for 5 min at that temperature, 0.35 ml (4.54 mmol) of methyl chloroformate were slowly added and stirring was continued for 5 more min. The yellow solution turned bright orange after the addition of the chloroformate. Quenched with 1 M HCl at −78 °C, the solution was then allowed to warm to room temperature. The aqueous phase was separated and extracted with diethyl ether, and the combined organic portions were washed with brine, dried over $MgSO_4$, filtered and evaporated under reduced pressure. Chromatography on silica gel using hexanes–ethyl acetate (3 : 1 and then 1 : 1) furnished 684 mg of pure product **14** and 445 mg of a 1 : 1 mixture of product and starting material for a total yield of 85% based on the quantity of methyl chloroformate; δ_H(250 MHz, $CDCl_3$) 7.17 (dt, 1H, *J* 1.1, 2.6), 4.80 (br s, 1H), 3.96–4.15 (m, 2H), 3.83 (s, 3H), 3.79 (s, 3H); *m*/*z* (EI) 234 (23%, M^+) (HRMS calc. for $C_8H_{10}O_6S$: 234.0198. Found: 234.0189).

1,2-Bis(methoxycarbonyl)buta-1,3-diene 15

2,3-Bis(methoxycarbonyl)-3-sulfolene **14** (50 mg, 0.21 mmol) was stirred in 3 ml of dry toluene and heated to reflux for 12 h. The solvent was then removed under reduced pressure and the product directly chromatographed on silica gel using hexanes–ethyl acetate (8 : 1 and then 3 : 1) to give 36 mg of isomer **A** and 17 mg of isomer **B**. Both were slightly volatile. The proton NMR spectrum of the crude mixture, however, indicated a 1 : 1 mixture of the two volatile compounds. The less polar **A** was identified as the (*E*)-isomer because some of it was recovered after the mixture was reacted with maleic anhydride in a Diels–Alder reaction. In addition, its signal at δ 6.35 must be that of a vinyl proton *cis* to a carbonyl. The same signal for the (*Z*)-isomer is found at δ 5.86. Less polar (*E*)-isomer **A**: δ_H(250 MHz, $CDCl_3$) 7.44 (ddd, 1H, *J* 1.4, 10.5, 16.9), 6.35 (br s, 1H), 5.89 (dm, 1H, *J* 16.9), 5.60 (dt, 1H, *J* 1.4, 10.5), 3.82 (s, 3H), 3.75 (s, 3H); *m*/*z* (EI) 170 (35%, M^+) (HRMS calc. for $C_8H_{10}O_4$: 170.0579. Found: 170.0584). More polar (*Z*)-isomer **B**: δ_H(250 MHz, $CDCl_3$) 6.37 (dd, 1H, *J* 10.6, 17.5), 5.86 (br s, 1H), 5.54 (d, 1H, *J* 10.6), 5.49 (d, 1H, *J* 17.5), 3.88 (s, 3H), 3.71 (s, 3H).

Cycloadduct 16

An equimolar mixture of (*E*)- and (*Z*)-2,3-bis(methoxycarbonyl)-3-sulfolene **14** (50 mg, 0.21 mmol) and maleic anhydride (71 mg, 0.73 mmol) in 3 ml of dry toluene was stirred and heated to reflux for 12 h. The solvent was then removed under reduced pressure but the product proved labile on silica chromatography. The isomeric mixture was characterised as the crude mixture. Both isomers: δ_H(250 MHz, $CDCl_3$) 7.28 (dd, 1H, *J* 2.7, 7.8), 7.2–7.3 (m, 1H), 4.64 (d, 1H, *J* 6.1), 4.52 (br s, 1H), 4.05 (dd, 9.9 Hz), 3.80 (s, 3H), 3.77 (s, 3H), 3.68 (s, 3H), 3.63 (s, 3H), 3.31–3.25 (m, 2H), 3.0–2.8 (m, 1H), 2.46 (ddd, 1H, *J* 0.5, 7.4, 17.2), 2.6–2.5 (m, 1H), 2.46 (ddd, 1H, *J* 3.0, 5.6, 17.2). One signal from one isomer is missing, believed buried under the ester peaks.

Cycloadduct 17

An equimolar mixture of (*E*)- and (*Z*)-2,3-bis(methoxycarbonyl)-3-sulfolene **14** (50 mg, 0.21 mmol) and 1-morpho-

linocyclopentene (65 mg, 0.43 mmol) in 3 ml of dry toluene was stirred and heated to reflux for 12 h. The solvent was then removed under reduced pressure and the product directly chromatographed on silica gel using hexanes–ethyl acetate (8 : 1 and then 3 : 1) as eluent to yield 17 mg of pure cycloadduct **17** and 31 mg of mostly compound **17** contaminated with some morpholine adduct **18**. Only **17** was fully characterised since **18** eliminates the morpholine moiety upon further chromatography. δ_H(360 MHz, $CDCl_3$) 7.59 (br s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.06 (m, 1H), 2.93 (dt, 4H, *J* 7.3, 15.0), 2.08 (quin, 2H, *J* 7.3), 2.1–1.5 (m, 2H) [the last 2 protons are among a small amount of inseparable impurity and it is difficult to assign them]; δ_C(75.7 MHz, $CDCl_3$) 169.6 (s), 167.4 (s), 148.1 (s), 143.9 (s), 142.9 (s), 125.0 (d), 52.3 (q), 52.3 (q), 31.73 (t), 31.70 (t), 25.5 (t), 24.6 (t); ν_{max}($CHCl_3$)/cm^{-1} 1725 (br s), 1655 (s) cm^{-1}; *m*/*z* (EI) 236 (60%, M^+) (HRMS calc. for $C_{13}H_{16}O_4$: 236.1049. Found: 236.1046).

Adduct from 1-methoxycarbonylbuta-1,3-diene and maleic anhydride

1-Methoxycarbonylbuta-1,3-diene (100 mg, 0.89 mmol) was mixed with maleic anhydride (262 mg, 2.67 mmol) and stirred at room temperature for several days. The reaction was followed by GC and after 15 h less than 50% product was formed (this is approximate since no standard was used). After several days, some starting diene still remained. The reaction could be pushed to completion by refluxing in toluene for 15 h and evaporating the solvent under reduced pressure. The resulting product was not amenable to chromatography and was only characterised by proton NMR analysis of the crude mixture; δ_H(250 MHz, $CDCl_3$) 6.2–6.1 (m, 2H), 3.65 (s, 3H), 3.65–3.50 (m, 2H), 3.5–3.35 (m, 1H), 2.5–2.4 (m, 2H).

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References

1 J. M. McIntosh and R. A. Sieler, *J. Org. Chem.*, 1978, **43**, 4431.
2 H. M. R. Hoffmann and J. Rabe, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 795.
3 W. Poly, D. Schomburg and H. M. R. Hoffmann, *J. Org. Chem.*, 1988, **53**, 3701.
4 L. K. Sydnes, L. Skattebøl, C. B. Chapleo, D. G. Leppard, K. L. Svanholt and A. S. Dreiding, *Helv. Chim. Acta*, 1975, **58**, 2061.
5 O. Goldberg and A. S. Dreiding, *Helv. Chim. Acta*, 1976, **59**, 1904.
6 A. I. D. Alanine, C. W. G. Fishwick, A. D. Jones and M. B. Mitchell, *Tetrahedron Lett.*, 1989, **30**, 5653.
7 M. E. Jung and C. N. Zimmerman, *J. Am. Chem. Soc.*, 1991, **113**, 7813.
8 C. Spino and J. Crawford, *Can. J. Chem.*, 1993, **71**, 1094.
9 H.-J. Liu, T. K. Ngooi and E. N. C. Browne, *Can. J. Chem.*, 1988, **66**, 3143.
10 D. Martina and F. Brion, *Tetrahedron Lett.*, 1982, **23**, 865.
11 H. Düttmann and P. Weyerstahl, *Chem. Ber.*, 1979, **112**, 3480.
12 B. Tarnchompoo, C. Thebtaranonth and Y. Thebtaranonth, *Tetrahedron Lett.*, 1987, **28**, 6671.
13 J. F. Honek, M. L. Mancini and B. Belleau, *Synth. Commun.*, 1984, **14**, 483.
14 M. Franck-Neumann, D. Martina and M.-P. Heitz, *J. Organomet. Chem.*, 1986, **301**, 61.
15 T.-S. Chou and S.-C. Hung, *J. Org. Chem.*, 1988, **53**, 3020.
16 M. Franck-Neumann, D. Martina and F. Brion, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 864.
17 R. F. Borch, *J. Org. Chem.*, 1969, **34**, 627.
18 R. L. Crumbie and D. D. Ridley, *Aust. J. Chem.*, 1981, **34**, 1017.
19 T.-S. Chou, C.-Y. Tsai and L.-J. Huang, *J. Org. Chem.*, 1990, **55**, 5410.
20 I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, Wiley Interscience, Chichester, 1976.
21 T. A. Nguyên, *Orbitales frontières*, *Manuel pratique*, Interéditions, CNRS éditions, Paris, 1995.
22 E. L. Eliel and S. H. Wilen, *Stereochemistry of Organic Compounds*, Wiley, New York, 1994.
23 E. Juaristi, *Stereochemistry & Conformational Analysis*, Wiley Interscience, New York, 1991.
24 K. N. Houk, Y. Li and J. D. Evanseck, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 682.
25 Y. Li and K. N. Houk, *J. Am. Chem. Soc.*, 1993, **115**, 7478.
26 K. N. Houk, *J. Am. Chem. Soc.*, 1973, **95**, 4092.
27 P. G. Baraldi, A. Barco, S. Benetti, S. Manfredini, G. P. Pollini, D. Simoni and V. Zanirato, *Tetrahedron*, 1988, **44**, 6451.
28 G. L. Dunn and J. K. Donohue, *Tetrahedron Lett.*, 1968, 3485.
29 R. D. Brown, *J. Chem. Soc.*, 1950, **2**, 691.
30 Streitwieser, *Molecular Orbital Theory for Organic Chemists*, Wiley, New York, 1961.
31 V. D. Kiselev and A. I. Konovaloc, *Russ. Chem. Rev.*, 1988, **58**, 230.
32 R. E. Townsend, G. Ramunni, L. E. Overmann, W. J. Hehre and L. Salem, *J. Am. Chem. Soc.*, 1976, **98**, 2190.
33 R. D. Bach, J. J. W. McDouall and H. B. Schlegel, *J. Org. Chem.*, 1989, **54**, 2931.
34 W. Carruthers, *Cycloaddition Reactions in Organic Synthesis*, ed. J. E. Baldwin and P. D. Magnus, Pergamon Press, Oxford, 1991.
35 F. Fringuelli and A. Taticchi, *Dienes in the Diels–Alder Reaction*, Wiley, New York, 1990.

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