Pergamon

Tetrahedron Vol. 51, No. 46, pp. 12661-12666, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4020/95 $9.50+0.00

0040-4020(95)00806-3

Hetero-Diels-Alder Additions of Sulfur Dioxide to 1,3-Dienes: A Proposal for a New Reactive Diene from *ab initio* Calculations

Dimas Suárez, Emiliano Iglesias, Tomás L. Sordo, and José A. Sordo*

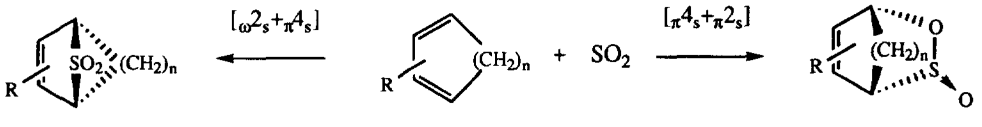
Departamento de Química Física y Analítica, Universidad de Oviedo, 33006 Oviedo, Principado de Asturias, Spain

Abstract: Ab initio calculations suggest that 1-methoxy-1,3-cyclohexadiene can be used to get a sultine when reacting with sulfur dioxide *via* a Diels-Alder reaction. The Cheletropic reaction (leading to a sulfolene) does not compete with the Diels-Alder cycloaddition either kinetically or thermodynamically.

INTRODUCTION

The $[_{\pi}4_s+_{\pi}2_s]$-cycloaddition of sulfur dioxide to 1,3-dienes is a rare reaction which has been reported in only a few of cases.[1-4] Recent ab initio calculations[5-7] and theoretical analysis[8] on the reaction between isoprene and sulfur dioxide have contributed to a deeper understanding of the mechanism through which such reactions proceed. In this paper we provide convincing theoretical arguments supporting the appropriateness of 1-methoxy-1,3-cyclohexadiene to be used as a reactive diene in order to get the corresponding sultine by means of a Diels-Alder cycloaddition.

Experimental evidence[3-4] and theoretical results[5-7] suggest that highly reactive dienes might be suitable for generating sultines, provided the hetero-Diels-Alder addition is not too slow and can be made to occur faster than the concurrent and more exothermic Cheletropic reaction to give a sulfolene.[3] Ab initio RHF/6-31G*//RHF/3-21G* calculations[9] were carried out to study the $[_{\omega}2_s+_{\pi}4_s]$ (Cheletropic) and $[_{\pi}4_s+_{\pi}2_s]$ (Diels-Alder) reactions of several highly reactive dienes (cyclopentadiene, 1,3-cyclohexadiene and 1-methoxy-1,3-cyclohexadiene) with sulfur dioxide (Scheme 1).



Scheme 1

Both thermal and Lewis acid-catalyzed (BH_3 was used as a model for the Lewis acid catalyst) reactions were considered. The analysis of the results suggested (see below) that 1-methoxy-1,3-cyclohexadiene could be an appropriate candidate to afford a sultine when reacting with sulfur dioxide. In order to reinforce the validity of that conclusion, keeping the computational cost within reasonable limits, higher level calculations (RHF/6-31G* optimizations) were carried out to study the reactions (Diels-Alder and Cheletropic) involving such a diene (single point MP2/6-31G*//RHF/6-31G* calculations are also reported). It has been shown previously that this theoretical level provides results that, for the type of systems and reactions involved in the present work, show a good accord with experimental data on reactivity, regioselectivity, and stereoselectivity.[7]

RESULTS AND DISCUSSION

The RHF/6-31G*//RHF/3-21G* transition structures[10] corresponding to the two stereoisomers (endo, exo) of the thermal Diels-Alder reactions of cyclopentadiene (**TS1**, **TS2**), 1,3-cyclohexadiene (**TS5**, **TS6**) and 1-methoxy-1,3-cyclohexadiene[11] (**TS9**, **TS10**) with sulfur dioxide, the two stereoisomers of the corresponding Lewis acid-catalyzed reactions (**TS3**, **TS4**; **TS7**, **TS8**; **TS11**, **TS12**), and the transition structures leading to sulfolenes through the alternative thermal (**TS17**-**TS21**) and Lewis acid-catalyzed (**TS18**-**TS22**) Cheletropic reactions were located by means of Schlegel's algorithm.[12] Also the different products of these reactions (**P1**-**P6**, **P9**-**P11**) were located and characterized. Table 1 collects the predicted activation energies and reaction energies for all the reactions considered. The corresponding values for the reactions between isoprene and sulfur dioxide (**TS13**-**TS16**, **TS23**-**TS24**, **P7**-**P8**, **P12**) are also included for comparative purposes. The RHF/6-31G* activation energies and reaction energies of the Diels-Alder and Cheletropic reactions between 1-methoxy-1,3-cyclohexadiene and sulfur dioxide (**TS25**-**TS30**, **P13**-**P15**) are given in Table 2 (values in parentheses correspond to the reactions between isoprene and sulfur dioxide).[5,7] Figure 1 depicts the transition structures **TS25**-**TS30**.[13]

Cyclopentadiene was chosen in the present study because it is known to be a highly reactive diene in Diels-Alder reactions. Data collected in Table 1 corroborate this point (in the following discussion we will refer to the results on the Lewis acid-catalyzed reactions. It should be noted that consideration of the results on the thermal reactions leads to the same conclusions). Indeed, the activation energies of the two stereoisomers **TS3** (10.6 kcal/mol) and **TS4** (12.4 kcal/mol) are lower than those for isoprene (**TS15**: 13.6 kcal/mol, **TS16**: 18.4 kcal/mol) which has been shown to be one of the scarce dienes that react with sulfur dioxide to give a sultine.[3] On the other hand, contrary to isoprene, cyclopentadiene gives rise to a sulfolene (*via* Cheletropic reaction) which results to be thermodynamically less stable than the corresponding sultine (compare **P9**: 28.4 kcal/mol with **P1**: 2.6 kcal/mol). That means that, for the case of cyclopentadiene, the Cheletropic reaction does not compete with the Diels-Alder cycloaddition either kinetically or thermodynamically. However, the reaction energy for the Diels-Alder reaction of cyclopentadiene with sulfur dioxide (**P1**: 2.6 kcal/mol), when compared with that of isoprene (**P12**: -13.0 kcal/mol), indicates that the sultine formed will be unstable (strained structure) and will undergo fast cycloreversion.

In order to overcome this problem, the 1,3-cyclohexadiene was considered. According to expectations, the Diels-Alder reaction becomes substantially more exothermic (**P3**: -3.4 kcal/mol) than that with cyclopentadiene (**P1**: 2.6 kcal/mol). The activation energy becomes sligthly larger (**TS7**: 13.3 kcal/mol *vs.* **TS3**: 10.6 kcal/mol) but still remaining lower than that for the case of isoprene (**TS15**: 13.6 kcal/mol). On the other hand, although the sulfolene formed by the Cheletropic reaction involving 1,3-cyclohexadiene becomes more stable (**P10**: 6.6 kcal/mol) than that from cyclopentadiene (**P9**: 28.4 kcal/mol), it is definitively much less stable than the corresponding sultine (**P3**: -3.4 kcal/mol). All this data suggest that 1,3-cyclohexadiene should render the corresponding sultine when being mixed with sulfur dioxide under the conditions reported in reference 3.

Table 1. RHF/6-31G*//RHF/3-21G* Calculated Energies (kcal/mol) of the Transition Structures and Products Relative to Reactants for the Diels-Alder and Cheletropic reactions of cyclopentadiene (**1**), 1,3-cyclohexadiene (**2**), 1-methoxy-1,3-cyclohexadiene (**3**), and isoprene (**4**) with sulfur dioxide.

DIELS-ALDER					
Transition Structures		ΔE	**Transition Structures**		ΔE
1 + SO_2 (endo)	**TS1**	26.4	**1** + SO_2-BH_3 (endo)	**TS3**	10.6
1 + SO_2 (exo)	**TS2**	27.5	**1** + SO_2-BH_3 (exo)	**TS4**	12.4
2 + SO_2 (endo)	**TS5**	29.2	**2** + SO_2-BH_3 (endo)	**TS7**	13.3
2 + SO_2 (exo)	**TS6**	31.8	**2** + SO_2-BH_3 (exo)	**TS8**	17.6
3 + SO_2 (endo-meta)	**TS9**	19.3	**3** + SO_2-BH_3 (endo-meta)	**TS11**	1.8
3 + SO_2 (exo-meta)	**TS10**	21.3	**3** + SO_2-BH_3 (exo-meta)	**TS12**	4.1
4 + SO_2 (endo-meta)	**TS13**	29.2	**4** + SO_2-BH_3 (endo-meta)	**TS15**	13.6
4 + SO_2 (exo-meta)	**TS14**	32.3	**4** + SO_2-BH_3 (exo-meta)	**TS16**	18.4
Products					
1 + SO_2 (endo)	**P1**	2.6			
1 + SO_2 (exo)	**P2**	1.6			
2 + SO_2 (endo)	**P3**	-3.4			
2 + SO_2 (exo)	**P4**	-3.6			
3 + SO_2 (endo-meta)	**P5**	-4.6			
3 + SO_2 (exo-meta)	**P6**	-4.2			
4 + SO_2 (endo-meta)	**P7**	-13.0			
4 + SO_2 (exo-meta)	**P8**	-9.5			
CHELETROPIC					
Transition Structures		ΔE	**Transition Structures**		ΔE
1 + SO_2	**TS17**	37.5	**1** + SO_2-BH_3	**TS18**	33.7
2 + SO_2	**TS19**	37.6	**2** + SO_2-BH_3	**TS20**	30.0
3 + SO_2	**TS21**	33.9	**3** + SO_2-BH_3	**TS22**	16.2
4 + SO_2	**TS23**	37.9	**4** + SO_2-BH_3	**TS24**	26.3
Product					
1 + SO_2	**P9**	28.4			
2 + SO_2	**P10**	6.6			
3 + SO_2	**P11**	17.0			
4 + SO_2	**P12**	-12.8			

To enhance the reactivity of 1,3-cyclohexadiene, the 1-methoxy-1,3-cyclohexadiene was considered. Data collected in Table 1 strongly support the expectations. Indeed, from the thermodynamic viewpoint, the sultine obtained is more exothermic (**P5**: -4.6 kcal/mol) than that from 1,3-cyclohexadiene (**P3**: -3.4 kcal/mol) while the corresponding sulfolene becomes remarkably less stable (**P11**: 17.0 kcal/mol *vs*. **P10**: 6.6 kcal/mol). From the kinetic viewpoint, the activation barrier for the Diels-Alder reaction becomes notably lower (**TS11**: 1.8 kcal/mol *vs*. **TS7**: 13.3 kcal/mol).

In agreement with our previous findings,[7] higher level calculations (RHF/6-31G* optimizations) do support the validity of our conclusions. Data collected in Table 2 corroborate that from the thermodynamic viewpoint the sultine obtained when reacting 1-methoxy-1,3-cyclohexadiene with sulfur dioxide (**P13**; -2.0 kcal/mol), although less stable than that from isoprene (-9.5 kcal/mol), becomes definitively much more stable than the corresponding sulfolene (**P15**; +19.9 kcal/mol).[14] From the kinetic viewpoint, the activation barrier for the Lewis acid-catalyzed Diels-Alder reaction (**TS27**; 7.4 kcal/mol), which is notably lower than in the case of isoprene (19.4 kcal/mol), becomes clearly lower than that for the Cheletropic reaction (**TS30**; 24.2 kcal/mol). All the above means that, for the case of 1-methoxy-1,3-cyclohexadiene, the Cheletropic reaction does not compete with the Diels-Alder cycloaddition either kinetically or thermodynamically.

Table 2. Calculated Energies (kcal/mol) of the RHF/6-31G* Optimized Transition Structures and Products Relative to Reactants for the Diels-Alder and Cheletropic reactions of 1-methoxy-1,3-cyclohexadiene (**3**) with sulfur dioxide. Figures in parentheses correspond to the reaction between isoprene and sulfur dioxide.

DIELS-ALDER			
Transition Structures		ΔE	ZPVE[a]
3 + SO_2 (endo-meta)	**TS25**	17.3 (28.2)	1.6 (1.8)
3 + SO_2 (exo-meta)	**TS26**	19.4 (31.7)	1.7 (1.5)
3 + SO_2-BH_3 (endo-meta)	**TS27**	4.1 (15.7)	3.3 (3.7)
3 + SO_2-BH_3 (exo-meta)	**TS28**	5.9 (20.3)	3.3 (3.4)
Products			
3 + SO_2 (endo-meta)	**P13**	-5.2 (-13.9)	3.2 (4.4)
3 + SO_2 (exo-meta)	**P14**	-5.1 (-10.4)	3.3 (4.2)
CHELETROPIC			
Transition Structures		ΔE	ZPVE[a]
3 + SO_2	**TS29**	32.8 (37.5)	1.8 (1.7)
3 + SO_2-BH_3	**TS30**	19.9 (28.8)	4.3 (3.9)
Product			
3 + SO_2	**P15**	16.5 (-13.0)	3.4 (4.3)

[a] HF/6-31G* zero point energy correction to the relative energies.

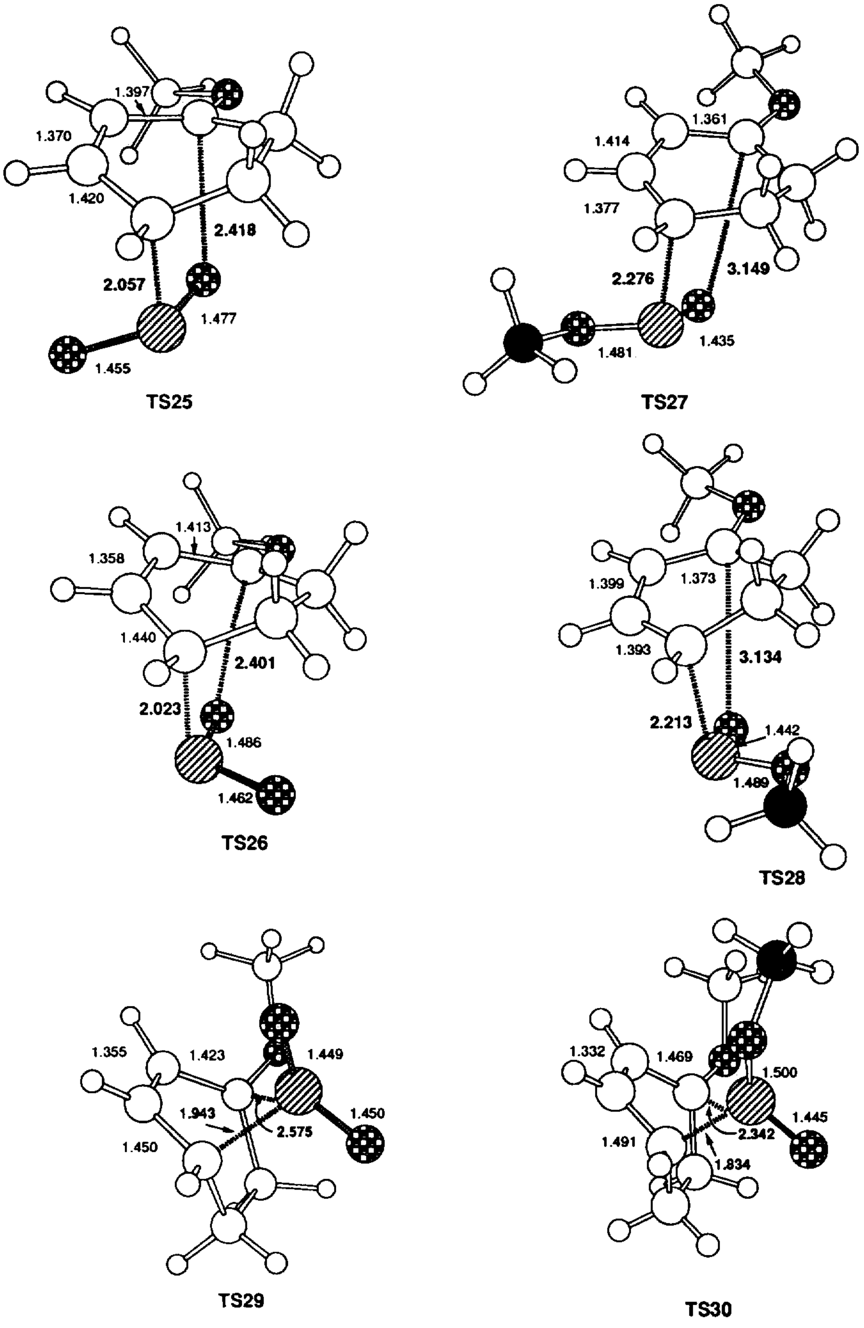


Fig. 1. RHF/6-31G* transition structures for thermal and Lewis acid-catalyzed (Diels-Alder and cheletropic) reactions of 1-methoxy-1,3-cyclohexadienene with sulfur dioxide.

CONCLUSION

As a conclusion, ab initio calculations predict that the Diels-Alder reaction of 1-methoxy-1,3-cyclohexadiene with sulfur dioxide shoud proceed to give the corresponding sultine in a similar way as that reported recently for the cases of isoprene and (E)-piperylene.[3] We hope the theoretical results reported in this paper will stimulate experimental work to validate our predictions.

REFERENCES AND NOTES

1. Heldeweg, R.F.; Hogeveen, H. J. Am. Chem. Soc. **1976**, 98, 2341.
2. Durst, T.; Tétreault-Ryan, L. Tetrahedron Lett. **1978**, 2353.
3. Deguin, B.; Vogel, P. J. Am. Chem. Soc. **1992**, 114, 9210.
4. Deguin, B.; Vogel, P. Tetrahedron Lett. **1993**, 34, 6269.
5. Suárez, D.; Sordo, T.L.; Sordo, J.A. J. Am. Chem. Soc. **1994**, 116, 763.
6. Suárez, D.; Assfeld, X.; González, J.; Ruiz-López, M.F.; Sordo, T.L.; Sordo, J.A. J. Chem. Soc. Chem. Commun. **1994**, 1683.
7. Suárez, D.; González, J.; Sordo, T.L.; Sordo, J.A. J. Org. Chem. **1994**, 59, 8058. Suárez, D.; Sordo, T.L.; Sordo, J.A. J. Org. Chem. **1995**, 60, 2848. Suárez, D.; López, R.; González, J.; Sordo, T.L.; Sordo, J.A. Int. J. Quantum Chem. (in press).
8. The configurational analysis based on the expansion of the MOs of a complex system in terms of the MOs of its fragments, developed by our group for three-molecule interactions has proved quite useful, specially in the study of catalyzed reactions: Menéndez, M.I.; Sordo, J.A.; Sordo, T.L. J. Phys. Chem. **1992**, 96, 1185. Menéndez, M.I.; López, R.; Suárez, S.; Sordo, T.L.; Sordo, J.A. Comput. Phys. Commun. **1993**, 76, 235. Menéndez, M.I.; González, J.; Sordo, J.A.; Sordo, T.L. J. Mol. Struct. (Theochem) **1994**, 309, 295. Menéndez, M.I.; Suárez, D.; Sordo, J.A.; Sordo, T.L. J. Comput. Chem. **1995**, 16, 659.
9. The calculations were performed using the GAUSSIAN 92 package of programs: Frisch, M.J.; Trucks, G.W.; Head-Gordon, M.; Gill, P.M.W.; Wong, M.W.; Foresman, J.B.; Johnson, B.G.; Schlegel, H.B.; Robb, M.A.; Replogle, E.S.; Gomperts, R.; Andres, J.L.; Raghavachari, K.; Binkley, J.S.; Gonzalez, C.; Martin, R.L.; Fox, D.J.; DeFrees, D.J.; Baker, J.; Stewart, J.J.P.; Pople, J.A. Gaussian Inc., Pittsburgh PA, 1992.
10. All the structures were fully optimized and characterized by performing vibrational frequency analysis.
11. Taking into account our previous studies (see references 5-7) only the regioisomer "meta" was considered for 1-methoxy-1,3-cyclohexadiene.
12. Schlegel, H.B. J. Comput. Chem. **1982**, 3, 211.
13. Geometrical parameters for the rest of structures computed, nor reported here for briefness, are available upon request.
14. It has been reported elsewhere (see reference 7) that correlation seems to be important in this regard. MP2/6-31G*//RHF/6-31G* single point calculations do confirm our conclusions (**P13**: -7.2(-9.1 kcal/mol), **P15**: 9.9 kcal/mol). However, it should be pointed out that the MP2/6-31G*//RHF/6-31G* energies obtained for the six transition structures **TS25-TS30** (8.8, 11.9, -11.3, -9.8, 18.0, and 1.9 kcal/mol, respectively) are clearly too much low. Unfortunately, the size of the systems involved makes the MP2/6-31G* level of theory unpractical.

(*Received in UK* 8 *September* 1995; *accepted* 21 *September* 1995)