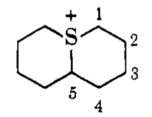
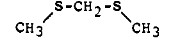
Table II. ^{13}C NMR Chemical Shifts of Salts 1a and 1b[a]



Carbon	1a	1b
1	38.3	30.7
2	23.9	20.0
3	23.5	19.9
4	30.7	26.1
5	53.3	42.6

[a] Spectra were determined on *ca.* 25% solutions in $CDCl_3$. Data are presented in ppm downfield from internal Me_4Si.

entropy terms. While $\Delta S^{\ddagger}$ for ylide **8** is more negative than $\Delta S^{\ddagger}$ for salt **7** by 4.5 eu, $\Delta S^{\ddagger}$ for ylide **4** is *more positive* than $\Delta S^{\ddagger}$ for salt **1** by 9.1 eu. Finally, it has recently been shown that conversion of 1,3-bissulfonium salt **9** to the corresponding ylide decreases $\Delta G^{\ddagger}$ for pyramidal inversion at sulfur by at least 5 kcal mol^{-1}.[12,13]



9

We are now engaged in studying the stereochemistry of the reaction of ylides **4a** and **4b** with various electrophiles.

Acknowledgment. This research was supported by a grant from the United States Public Health Service (No. AI-11607).

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(1) R. H. Eastman and G. Kritchevsky, *J. Org. Chem.*, **24**, 1428 (1959).
(2) Anal. Found: C, 44.19; H, 6.98; S, 12.89.
(3) R. F. Borch, *J. Org. Chem.*, **34**, 627 (1969).
(4) D. L. Tuleen and R. H. Bennett, *J. Heterocycl. Chem.*, **6**, 115 (1969).
(5) Anal. Found: C, 71.70; H, 8.79.
(6) Note that each carbon in the more stable sulfonium salt **1a** resonates downfield from the corresponding carbon in isomer **1b**, a situation parallel to that found in *trans*- and *cis*-decalin; J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, p 66.
(7) The precision of these parameters is obviously not high because of the difficulty of maintaining precise temperature control in this range and also because equilibration rates were determined at only two temperatures. However, treatment of the rates at −23 and −32 °C by the Eyring equation yields $\Delta G^{\ddagger}{}_{-23°}$ = 18.92 kcal mol^{-1} and $\Delta G^{\ddagger}{}_{-32°}$ = 18.97 kcal mol^{-1}, suggesting that the activation parameters are reasonably good.
(8) (a) D. Darwish and G. Tourigny, *J. Am. Chem. Soc.*, **88**, 4303 (1966); (b) R. Scartazzini and K. Mislow, *Tetrahedron Lett.*, 2719 (1967); (c) D. Darwish, *Mech. React. Sulfur Compd.*, **3**, 33 (1968); (d) A. Garbesi, N. Corsi, and A. Fava, *Helv. Chim. Acta*, **53**, 1499 (1970).
(9) D. Darwish and R. L. Tomilson, *J. Am. Chem. Soc.*, **90**, 5938 (1968).
(10) Extrapolated values.
(11) The free energy of activation of ylide **8** was calculated from the published rate constant, using the Eyring equation.
(12) S. Wolfe, P. Chamberlain, and T. F. Garrard, *Can. J. Chem.*, **54**, 2847 (1976).
(13) The $\Delta G^{\ddagger} \geq 25$ kcal mol^{-1} reported for salt **9** is highly approximate, having been determined from a single analysis at −10 °C. The $\Delta G^{\ddagger}$ = 19.7 kcal mol^{-1} for the derived ylide was determined at 2.4° by monitoring the equilibration at several points, although complete experimental data are not available.[12]

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MINDO/3 Study of the Addition of Singlet Oxygen ($^1\Delta_gO_2$) to 1,3-Butadiene

Sir:

The well-known[1] π-cycloaddition of singlet molecular oxygen ($^1\Delta_gO_2$, **1**) to conjugated dienes to form six-membered cyclic peroxides bears an obvious resemblance to the Diels-Alder reaction, and both processes were until recently thought to involve synchronous[2] pericyclic mechanisms. However McIver[3] has shown that π-cycloadditions are unlikely to involve symmetrical transition states and MINDO/3[4] studies[5] here have indeed shown that the transition states for several typical Diels-Alder reactions are very unsymmetrical,[6] one of the new bonds being almost completely formed, the other hardly at all. Our MINDO/3 calculations[9] for several reactions of **1** with olefins have moreover indicated that these are two-step[2] processes, involving peroxiranes or zwitterions as stable intermediates. We therefore felt it of interest to extend our MINDO/3 studies to the reaction of **1** with 1,3-butadiene (**2**).

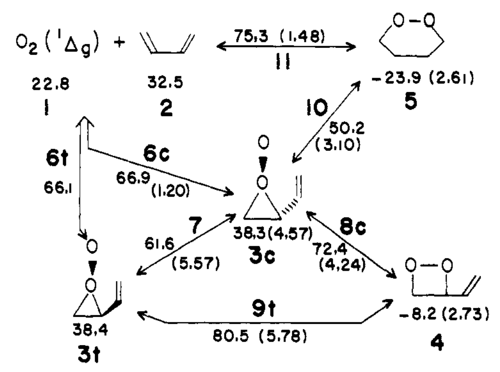

Figure 1. Heats of formation (kcal/mol) and dipole moments (D, in parentheses) of species involved in the reaction of $^1\Delta_g O_2$ with 1,3-butadiene and of transition states involved in their interconversions.

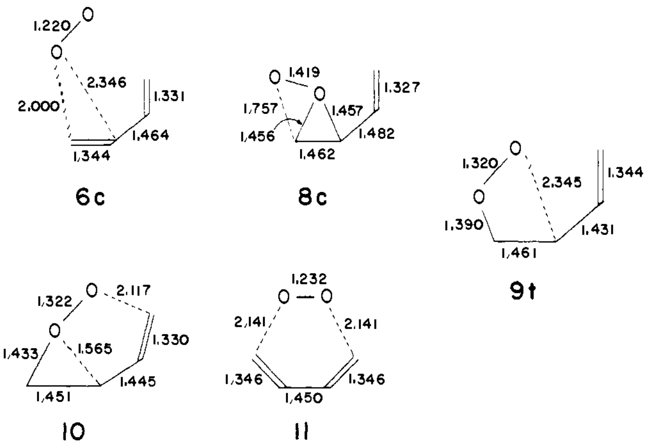

Figure 2. Geometries of transition states (bond lengths in Å).

Figure 1 shows the reactions we studied, using the techniques previously described.[9] The calculated heats of formation and dipole moments of the various stable species and transition states are also indicated in Figure 1 while Figure 2 shows the structures calculated for the transition states. These results imply that the first step in the reaction of **1** with **2** is the formation of a peroxirane which can exist as a cis (**3c**) or trans (**3t**) isomer. The activation energy for addition is 10.8 kcal/mol and the transition states (**6c**, **6t**) are reactant-like in their geometric and electronic structures. The intermediate *cis*-peroxirane (**3c**) can rearrange easily ($\Delta E^{\ddagger}$, 11.9 kcal/mol) to the cyclic peroxide **5**.

The overall activation energy for formation of **5** by this two-step route is less by 9.2 kcal/mol than by concerted 1,4-π-cycloaddition of **1** to **2**. This latter reaction could indeed be studied only by enforcing C_s symmetry. The corresponding "transition state" (**11**), while a stationary point on the potential surface, is *not* a true transition state because the force constant matrix has two negative eigenvalues (cf. ref 9 and 10).

The intermediates, **3c** and **3t**, can also rearrange to vinyldioxetane (**4**) via three different isomeric transition states that still retain the peroxirane structure. The easiest route, via **8c**, involves an activation energy of 34.1 kcal/mol, while reaction via the "open" transition state **9t** involves an activation energy of 42.2 kcal/mol (see Figure 2).

These results refer to single-determinant SCF calculations. Since the Diels-Alder reaction involves a biradicaloid[11] transition state and must consequently be treated with inclusion of CI_0,[12] we repeated the calculations for the species shown in Figure 1 in this way. The decreases in energy were less than 10 kcal/mol for all except **9t**, implying that the species have little biradical character and that the values without CI_0 should be accepted.[13] The same probably applies to **9t**, but this is irrelevant in the present connection. The activation energy for rearrangement of **3t** to **5** via **9t** remains greater than that for rearrangement to **5**, even when CI_0 is included.

Our calculations therefore imply that the π-cycloaddition of **1** to **2** is not only not synchronous but not even concerted, taking place in two steps via a stable intermediate peroxirane. This conclusion is of course subject to the uncertainties set by the limited accuracy of MINDO/3,[14] and it is also true that our estimate of the heats of formation of **3c** and **5** are probably too negative (see ref 9). Nevertheless we feel that our results provide quite strong support for the two-step mechanism of addition, which, it should be noted, is also consistent with the observed stereospecificity of the reactions of **1** with dienes.[1] In the two-step mechanism, stereochemistry could be lost only by rotation about either the exocyclic double bond or the CC bond in the peroxirane ring. Analogy shows that the activation energy for the former process must be at least 50 kcal/mol while that predicted by MINDO/3 for the latter is 27.9 kcal/mol. Both are much greater than the predicted barrier to rearrangement of **3c** to **5**.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Grant AFOSR 75-2749) and the Robert A. Welch Foundation (Grant F-126). The calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computation Center. One of us (W.T.) thanks the Studienstiftung des deutschen Volkes for a postdoctoral fellowship.

References and Notes

(1) For reviews of the Diels-Alder reaction between dienes and ${}^1\Delta_g\ \mathrm{O}_2$ see (a) K. Gollnick and G. O. Schenck in "1,4 Cycloaddition Reactions", J. Hamer, Ed., Academic Press, New York, N.Y., 1967, p 255; (b) D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971); (c) R. W. Denny and A. Nickon, *Org. React.*, **20**, 133 (1973).

(2) In our terminology, a *synchronous* reaction is one in which the various bond-forming and bond-breaking processes have occurred to comparable extents in the transition state. A *concerted* reaction is one that takes place in a single kinetic step. A *two-step* reaction is one involving a stable intermediate. A *two-stage* reaction is one that is concerted but not synchronous, some of the changes in bonding taking place between the reactants and the transition state, the rest between the latter and the products.

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(4) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285, 1294, 1302, 1307 (1975).

(5) M. J. S. Dewar, A. C. Griffin, and S. Kirschner, *J. Am. Chem. Soc.*, **96**, 6225 (1974).

(6) Recently Hehre et al.[7] have reported ab initio SCF calculations for the ethylene-butadiene Diels-Alder reaction which, they claim, show the transition state to be essentially symmetrical, contradicting the MINDO/3 calculations and also the arguments of McIver, to which they make no reference. A detailed reexamination[8] suggests that Hehre et al.[7] were correct in thinking that the reported[5] transition state corresponded to formation of an intermediate biradical from cyclohexene rather than a concerted π cycloaddition, but wrong in their claim that the overall reaction takes place in a single step via a symmetrical transition state.

(7) R. E. Townshend, G. Ramunni, G. Segal, W. J. Hehre, and L. Salem, *J. Am. Chem. Soc.*, **98**, 2190 (1976).

(8) M. J. S. Dewar and H. Rzepa, to be submitted for publication.

(9) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **97**, 3978 (1975).

(10) J. W. McIver and A. Komornicki, *J. Am. Chem. Soc.*, **94**, 2625 (1972).

(11) See M. J. S. Dewar, S. Kirschner, H. C. Kollmar, and L. E. Wade, *J. Am. Chem. Soc.*, **96**, 5242 (1974).

(12) CI_0 implies CI with the lowest doubly excited configuration; see R. C. Bingham and M. J. S. Dewar, *J. Am. Chem. Soc.*, **94**, 9107 (1972).

(13) Since allowance is made for electron correlation in MINDO/3 via the parametrization,[4] it is usually incorrect to include CI. This is required only in the case of biradical-like species where correlation between the two "unpaired" electrons becomes extreme. In such cases CI_0 commonly lowers the energy by >20 kcal/mol. Extensive tests here have shown that the energies calculated without CI are close to the truth if CI_0 lowers the energy by less than 15 kcal/mol.

(14) The average absolute error in the activation energies calculated by MINDO/3 for 30 miscellaneous reactions is 5 kcal/mol, less than the average error in calculated heats of formation of molecules studied in ref 4.

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Detection of Chirality with the Chemical Ionization Mass Spectrometer. "Meso" Ions in the Gas Phase

Sir:

While the mass spectrometer, or any other achiral physical probe, is unable to distinguish between optical isomers in the solid or liquid state, the strong interaction often found between pairs of enantiomers may be detected with such tools. Thus, it is well known that the melting point, solubility, and vapor pressure of racemic compounds are considerably different from those of their optically pure components.[1] As Zahorsky and Musso have shown,[2] if one of the enantiomers is isotopically labeled its preferential vaporization relative to the racemate is disclosed in its electron ionization mass spectrum by a change in the relative abundance of the two molecular ions with time. This same effect can be observed using chemical ionization

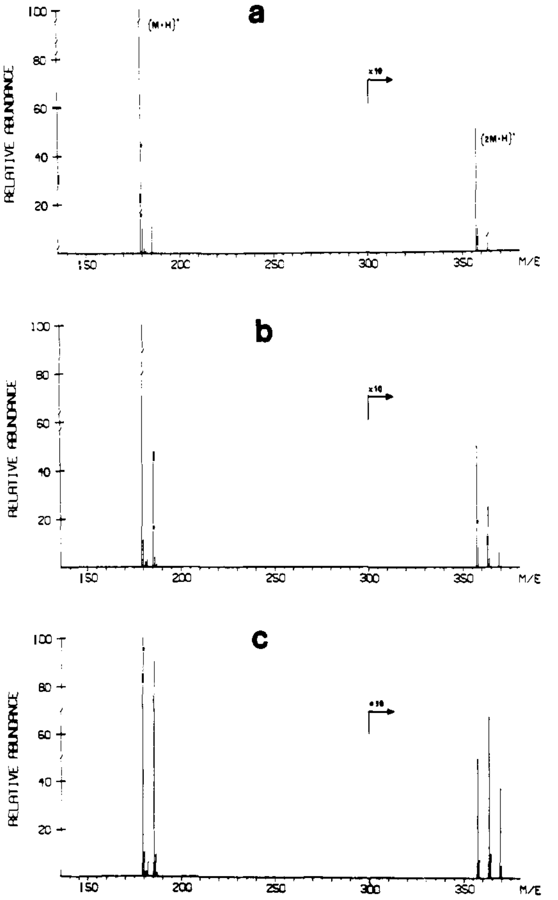

Figure 1. Dimethyl-d_6 D-tartrate (10%) and dimethyl-d_0 L-tartrate (90%) scanned sequentially, a through c.