dioxetane (**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 $^1\Delta_g O_2$ 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.

(3) J. W. McIver, Jr., *J. Am. Chem. Soc.*, **94**, 4782 (1972).

(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.

Michael J. S. Dewar,* Walter Thiel
Department of Chemistry, The University of Texas at Austin
Austin, Texas 78712

Received October 8, 1976

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

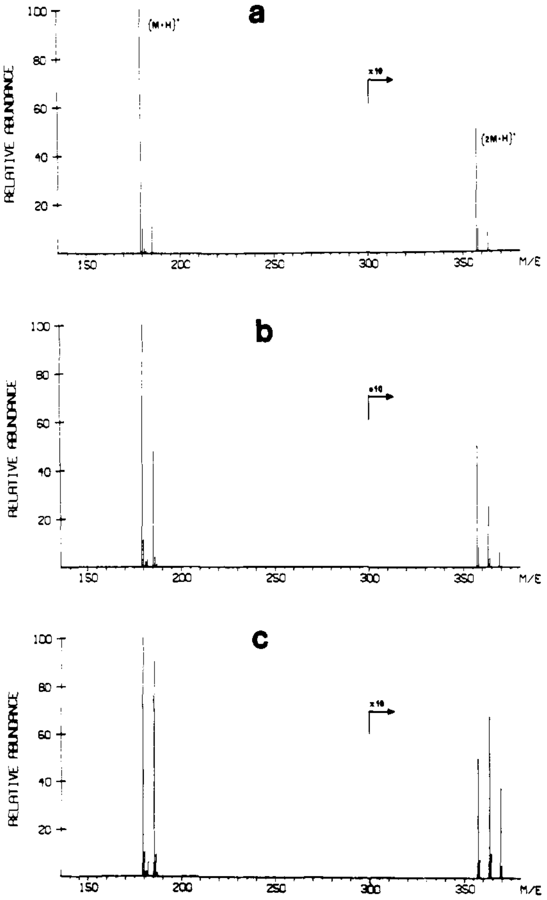

Figure 1. Dimethyl-d_6 D-tartrate (10%) and dimethyl-d_0 L-tartrate (90%) scanned sequentially, a through c.

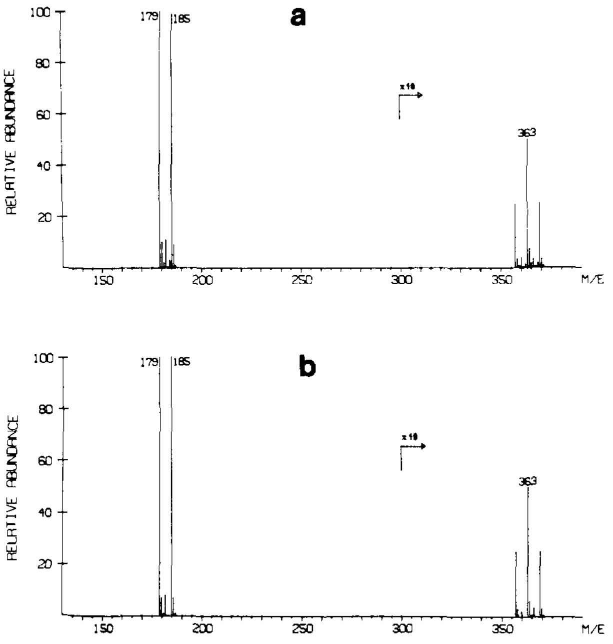

Figure 2. Dimethyl-d_0 D-tartrate (50%) and dimethyl-d_6 D-tartrate (50%) calculated (b) and found (a).

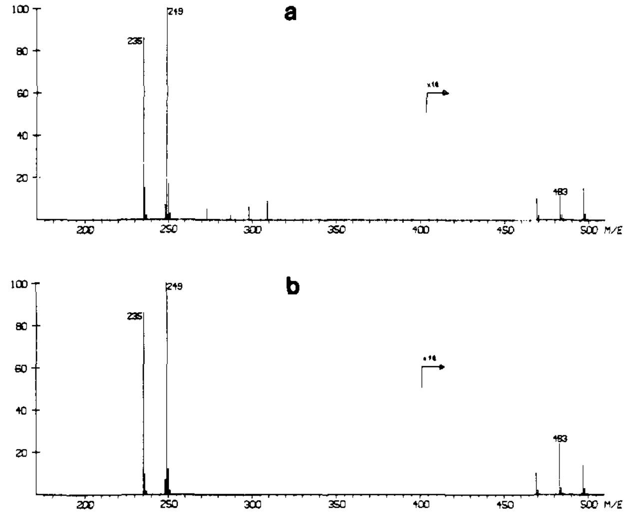

Figure 3. Diisopropyl-d_0 D-tartrate (50%) and diisopropyl-d_{16} L-tartrate (50%) calculated (b) and found (a).

mass spectrometry, as dimethyl tartrate[3] shows in a striking manner (Figure 1). With a mixture of 10% dimethyl-d_6 D-tartrate (MH^+ 185) and 90% dimethyl-d_0 L-tartrate (MH^+ 179) in the direct insertion probe, the excess optically active form preferentially evaporates, and the spectrum, corrected for incomplete deuteration, gradually approaches that expected for the pure racemate (Figure 1c).

However, inspection of the protonated dimer ($2M + H^+$) region reveals another effect due to chirality that is *independent* of the physical interactions between optical isomers in the liquid or solid state. Thus ratios of the intensities of the peaks in this region should obey the quadratic relation $(d_0L + d_6D)^2$, i.e., if D and L components are equally abundant as expected for a racemate, they should exhibit a 1:2:1 pattern of d_0L–d_0L, d_0L–d_6D, and d_6D–d_6D protonated dimer ions, respectively. However, close inspection of Figure 1c, where the ions reflect a nearly racemic composition of the sample, reveals a central peak due to the "meso"[4] ion that is only 78% of the value calculated from the ions at *m/e* 357 and 369. On the other hand, when equimolar mixtures of dimethyl-d_0D- and -d_6 D-tartrate are examined, the expected 1:2:1 pattern is indeed observed (Figure 2), ruling out isotope effects in the experiment.[5] This effect is even more dramatically exhibited by mixtures of diisopropyl-d_0 D-tartrate and its -d_{14} L isomer (Figure 3), where the central peak in the $2M + H^+$ region is now only 46% of the calculated value. Since the effect only compares DD (or LL) with DL interactions, it is difficult to say whether it is caused by stronger bonding in the former (for example through multiple points of attachment) or steric hindrance in the latter. In any case, the interactions responsible must be quite unique since no similar effect was detected in the cases of D-camphor and L-camphor-*3,3*-d_2 and of *N*-acetyl-D-amphetamine and *N*-acetyl-d_3-L-amphetamine.

While the analytical utility of this effect would seem to be minimal, it does provide a tool to investigate certain structural features of these collision-stabilized $2M + H^+$ ions in chemical ionization mass spectrometry. For example, it is clear that in such cases chirality must be preserved in at least a corresponding fraction of the $2M + H^+$ ions. Furthermore, there seems to be no reason, a priori, that only relative *destabilization* of the "meso" ion should be found; indeed the opposite might have been predicted from the melting points of the dimethyl tartrates.[3] We are currently searching for further examples of this interesting effect, particularly outside of the tartrate class, in order to gain more insight into its structural requirements.

References and Notes

(1) A. Findlay and A. N. Campbell, "The Phase Rule and Its Applications", Dover, New York, N.Y., 1945, pp 136, 256.
(2) U.-I. Zahorsky and H. Musso, *Chem. Ber.*, **106**, 3608 (1973).
(3) We selected dimethyl tartrate because the unusually high congruent melting point of its racemate (90 °C) compared to its enantiomers (48, 50, or 61 °C, J. H. Adriani, *Z. Phys. Chem.*, **33**, 453 (1900).) suggested the presence of interactions in the racemic crystal that might result in a sublimation vapor pressure less than that of the crystalline enantiomers.
(4) We use the term "meso" ion without its usual implication of symmetry. All we know of these ions is that they are composed of one D and one L molecule combined with a proton. The actual structures present in an assemblage of such ions can be visualized as being either true meso (i.e., having a plane, center or alternating axis of symmetry), or mixtures of equal numbers of still asymmetric ions.
(5) One of our referees has pointed out that the difference in free energy between the dimers represented by Figure 1c and theory is only ca. −0.16 kcal/mol, about what might be expected for a hydrogen–deuterium isotope effect, so the d_0-D-d_6-D experiment in Figure 2 is especially important.

H. M. Fales*
National Heart, Lung, and Blood Institute
National Institutes of Health
Bethesda, Maryland 20014

G. J. Wright
Chemistry Department
University of Canterbury
Christchurch, New Zealand

Received August 31, 1976

Aza Analogy to Singlet Oxygen. The Simultaneous Stereospecific Functionalization of the Four Cyclopentadiene sp^2 Carbon Atoms by Reaction with Nitrosochloroethylenes

Sir:

Nitro[1] and nitroso[2] activated acetylenes and chloroethylenes **1** as their formal hydrochlorides[3,4] have been studied in our laboratories as versatile electron deficient synthons. The nitroso group is known to function as a dienophile,[5-7] and thus is analogous to singlet oxygen,[8-10] particularly when the nitroso function is attached to electronegative groups as in **1**. In fact