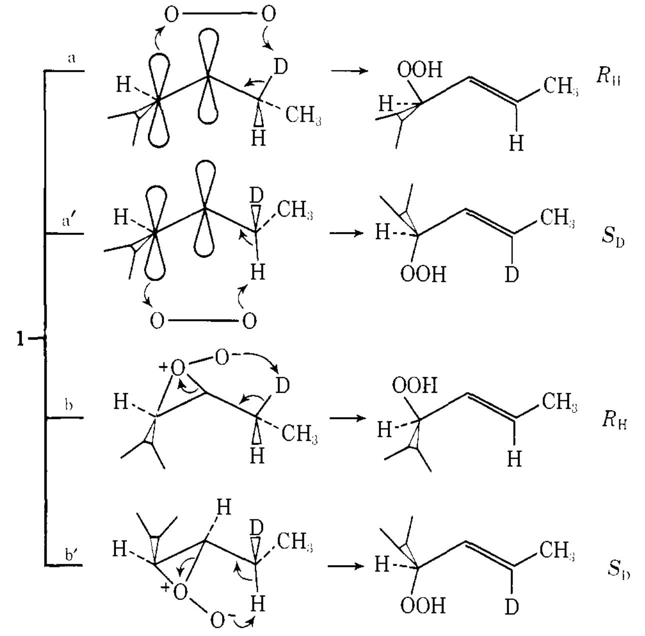
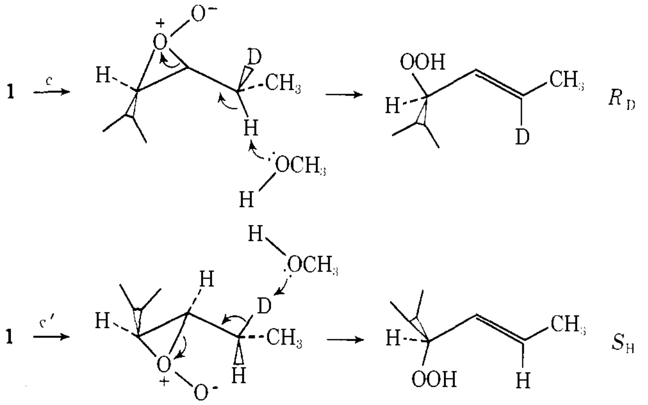
Nickon, *et al.*,[9] and Kopecky, *et al.*,[10] have also found small isotope effects in singlet oxygen reactions. Such results have been interpreted, particularly by Nickon, to support the concerted ene mechanism with hydrogen (deuterium) abstraction occurring late on the reaction coordinate.



The results obtained by treating olefin **1** with singlet oxygen in methanol make the concerted ene mechanism more difficult to accept[11] (see Table I). The D/H ratios now no longer match the *S*/*R* ratios, primarily due to the appearance of product R_D at the expense of R_H.

This uncoupling of the enantiomeric and isotopic ratios alone is difficult to understand within the framework of the concerted ene mechanism. The results can, however, be accommodated to the perepoxide mechanism by employing the more basic protic solvent methanol in an assisted β elimination as shown below.



The mechanisms displayed, c and c′, competing with unimolecular reorganizations (b and b′) could clearly generate the larger isotope effects found. Note that when solvent removal of a proton in a trans β elimination (c) competes with deuterium removal by path b, sizable quantities of solvent-derived product, R_D, are found. On the other hand, when the competition is reversed and solvent removal of deuterium competes with intramolecular proton abstraction, little or no solvent-derived product, S_H, can be found. This would appear to be a sensible expectation.

In summary, we believe that the results presented are not consistent with a conventional picture[14] of a concerted ene mechanism. These experiments likewise provide no *direct* evidence in support of the perepoxide intermediate. We feel that our results most reasonably require irreversible attack on the double bond as the rate-determining step in this reaction. The perepoxide formulation is used here for illustrative purposes only, but we believe that it provides a satisfactory picture of this reaction. Charge transfer or π complexes between olefin and singlet oxygen might also be proposed to explain these results.

Finally, it should be noted that these results may be peculiar to relatively unreactive disubstituted olefins. The methods outlined here are obviously applicable to more highly substituted systems and to other ene-type reactions; such approaches are currently under investigation.

Acknowledgment. The authors wish to thank H. S. Mosher for helpful comments. The work was supported by a Merck Award for Faculty Development and by the Dreyfus Foundation through a Camille and Henry Dreyfus Teacher–Scholar Grant. P. K. S. was supported *via* the generosity of Du Pont and Company and D. E. M. *via* the generosity of a Frederick P. Whitaker Fellowship.

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[9] A. Nickon, *et al.*, *J. Amer. Chem. Soc.*, **94**, 5517 (1972).

[10] K. R. Kopecky, J. H. van de Sande, and C. Mumford, *Can. J. Chem.*, **46**, 25 (1968).

[11] The ratio of products **2**, **3**, and **4** observed in acetone is very close to those reported earlier for similar olefins.[12] This product ratio and the absence of the isomers of compound **2**, R_D and S_H in the acetone solvent experiments, serve to establish the intermediacy of singlet oxygen and the absence of radical-chain oxidations. In methanol, the absence of isomer S_H and the ratio of products **2**, **3**, and **4** again argues against radical-chain reactions. This contention was checked by examining the rate change exhibited when CH_3OH was replaced by CD_3OD. Results similar to those reported by Kearns[13] were found, again implicating singlet oxygen as the reactive intermediate.

[12] C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

[13] P. B. Merkel, R. Nilsson, and D. B. Kearns, *J. Amer. Chem. Soc.*, **94**, 1030 (1972).

[14] We note that the result in acetone can be explained by a concerted ene transformation with a small isotope effect and that the result in methanol can be accommodated to a *mixture* of concerted mechanisms. We shall discuss this possibility along with a full description of these experiments.

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Molecular Beam Chemistry. Unimolecular Decomposition of Chemically Activated Chlorobromoalkyl Radicals

Sir:

In crossed-beam reactive scattering experiments, the time resolution is reduced to the duration of a single collision. When this is long compared to vibrational periods of the transient collision complex, the distributions in energy and angle of the reaction products provide information about the unimolecular decomposition of the complex.[1–4] The beam technique thus

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[1] W. B. Miller, S. A. Safron, and D. R. Herschbach, *Discuss. Faraday Soc.*, **44**, 108 (1967); *J. Chem. Phys.*, **56**, 3581 (1972).

[2] D. O. Ham and J. L. Kinsey, *J. Chem. Phys.*, **48**, 939 (1968); **53**, 285 (1970).

[3] J. M. Parson and Y. T. Lee, *J. Chem. Phys.*, **56**, 4658 (1972); J. M. Parson, K. Shobatake, Y. T. Lee, and S. A. Rice, *ibid.*, **59**, 1402 (1973).

[4] D. D. Parrish and D. R. Herschbach, *J. Amer. Chem. Soc.*, **95**, 6133 (1973), and references cited therein.

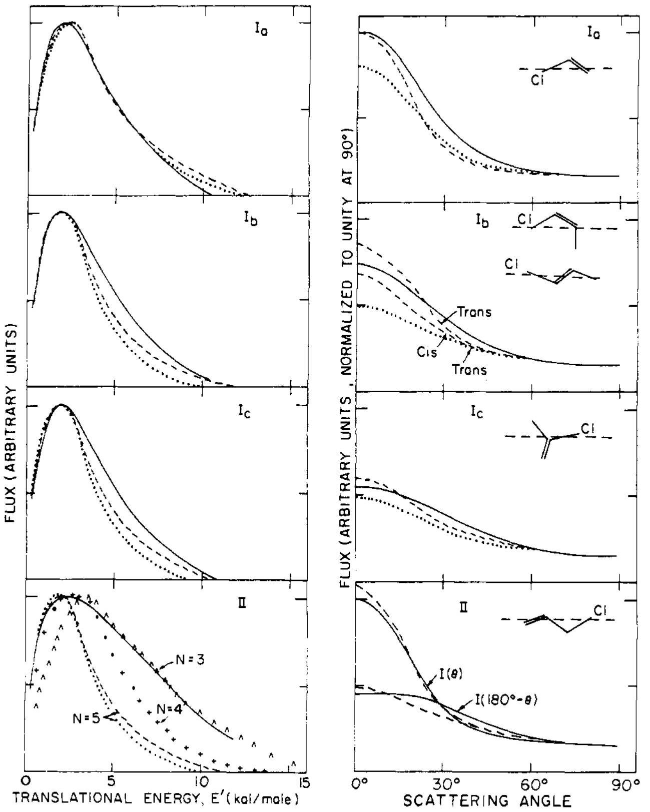

Figure 1. Distributions of product relative translational energy and scattering angle. Full curves from experimental data, others from transition-state models. The coordinate system has the center-of-mass as origin; direction of incident Cl atom is designated 0°, that of incident bromoolefin as 180°.

offers a single-collision version of the chemical activation method.[5] This is illustrated here with two types of displacement reactions

$$\text{Cl}\cdot + \text{RCH}{=}\text{CBrR}' \longrightarrow \text{RCH}{=}\text{CClR}' + \text{Br}\cdot \qquad (\text{I})$$

where (a) $R,R' = H,H$, (b) $R,R' = CH_3,H$, and (c) $R,R' = H,CH_3$ and

$$\text{Cl}\cdot + \text{CH}_2{=}\text{CHCH}_2\text{Br} \longrightarrow \text{CH}_2{=}\text{CHCH}_2\text{Cl} + \text{Br}\cdot \qquad (\text{II})$$

The product distributions are interpreted using a transition-state treatment[1,6] akin to the RRKM theory of unimolecular decomposition.[7] The distributions for the vinylic reaction I differ markedly from those for the allylic reaction II, indicating differences in the intramolecular energy exchange and transition states for the intermediate chlorobromoalkyl radicals.

Figure 1 shows the product translational energy distributions, $P(E')$, and angular distributions, $I(\theta)$. The experiments involve mass spectrometric detection and time-of-flight velocity analysis, as in previous work.[8] All four reactions have large cross sections, ~20–35 Å^2, and no detectable activation energy. In each case, the intermediate chlorobromoalkyl radical is vibrationally excited by ~29 kcal/mol, which is the sum of the initial collision energy (~4 kcal/mol), the mean thermal excitation of the reactant olefin (~2 kcal/mol), the loss in bond strength in converting the double bond to a single bond (~57 kcal/mol), and the gain in forming the new C–Cl bond (~80 kcal/mol). The total energy available to the products on re-forming the double bond and releasing the Br atom is ~18–20 kcal/mol.

The translational energy distributions for I correspond to random energy disposal in the intermediate radical, whereas that for II indicates a markedly nonrandom case. In the model calculations[6] shown in Figure 1 the principal factor is the density of vibration–rotation energy levels in the transition state.[9] The distributions calculated from the usual approximate quantum energy level density[10] assuming all degrees of freedom to be active (dotted curves) in intramolecular energy transfer are nearly the same as those calculated using the classical level density and neglecting the hydrogen atoms (dashed curves). Thus, even for a model based on energy randomization in the transition state, the quantum weighting makes the light H atoms "statistically inactive." For I all the heavy atoms (carbon or halogen) appear to be fully active, whereas for II less than half the heavy atom modes appear to be active.

The product angular distributions for all four reactions display the bimodal form characteristic of a collision complex.[1-4] The pronounced peaking at 0 and 180° shows that the centrifugal angular momentum of the chlorobromoalkyl radical is much larger than the rotational momentum of the reactant or product molecules, in accord with the large reaction cross sections.[1] Within experimental uncertainty, the $I(\theta)$ for reactions I are symmetric about 90°, indicating the chlorobromoalkyl radical persists for at least a few rotational periods, or $\gtrsim 5 \times 10^{-12}$ sec. For II, the $I(\theta)$ is quite asymmetric, with $I(0°)/I(180°) \gtrsim 3$, indicating an "osculating" complex[11] with mean lifetime less than a rotational period, or $\lesssim 1 \times 10^{-12}$ sec.

Figure 1 includes calculated $I(\theta)$ for "loose" and "tight" transition-state models.[7] The loose model[12] (dotted curves) allows free rotation of the incipient chloroolefin molecule and thus random migration of the Br atom. The tight model[13] (dashed curves) assumes the chloroolefin molecule has a preferred configuration with respect to the departing Br atom. This gives good agreement with experiment if the figure axis of the chloroolefin (rotational axis of least moment of inertia, pictured in Figure 1) lies along the direction of the Br atom within roughly ±30°. For Ib, comparable

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(5) B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, **3**, 1 (1964); E. A. Hardwidge, C. W. Larson, and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, **92**, 3278 (1970), and much work cited therein.

(6) S. A. Safron, N. D. Weinstein, D. R. Herschbach, and J. C. Tully, *Chem. Phys. Lett.*, **12**, 564 (1972).

(7) R. A. Marcus, *J. Chem. Phys.*, **43**, 2658 (1965), and references cited therein. For RRKM treatments of the decomposition of various chloroethyl radicals, see D. C. Tardy and B. S. Rabinovitch, *Trans. Faraday Soc.*, **64**, 1844 (1968); L. Huy, W. Forst, J. A. Franklin, and G. Huybrechts, *Chem. Phys. Lett.*, **3**, 307 (1969).

(8) J. D. McDonald, P. R. LeBreton, Y. T. Lee, and D. R. Herschbach, *J. Chem. Phys.*, **56**, 769 (1972).

(9) As described in ref 6 and 7, the level density involves a parameter $n = s + \frac{1}{2}r - 2$, where s and r denote respectively the number of active vibrational and rotational modes. For a tight transition state, $n = 3N - 7.5$, where N is the number of atoms. For a loose complex, $n = 3N - 8.5$. The curves shown in Figure 1 pertain to the tight case and those for $N = 3$ and $N = 4$ were calculated using the classical approximation.

(10) G. Z. Whitten and B. S. Rabinovitch, *J. Chem. Phys.*, **38**, 2466 (1963); D. C. Tardy, B. S. Rabinovitch, and G. Z. Whitten, *ibid.*, **48**, 1427 (1969).

(11) G. A. Fisk, J. D. McDonald, and D. R. Herschbach, *Discuss. Faraday Soc.*, **44**, 228 (1967); G. H. Kwei, A. B. Lees, and J. A. Silver, *J. Chem. Phys.*, **55**, 456 (1971); **58**, 1710 (1973).

(12) This is equivalent to the phase space theory of R. A. White and J. C. Light, *J. Chem. Phys.*, **55**, 379 (1971), and references cited therein. We thank D. A. Case for these calculations.

(13) In the notation of ref 1, the calculated curves correspond to $L_m \sim 220\hbar$, $M_0 \sim 27\hbar$, $M'_0 \sim 30\hbar$ and, for II, $\tau/\tau_r = 0.3$.

agreement is found for the trans and cis olefin conformations.

For both I and II the initial stage almost certainly involves attack on the double bond rather than the C–Br bond.[14] In view of the extensive evidence for anti-Markovnikov addition to olefins,[15] our reults suggest that I involves a facile 1,2-chlorine migration, probably with a bridged intermediate.[16] The product chloroolefin thus should have Cl on the carbon to which Br was originally bonded. This was verified for Ib and Ic by analysis of fragment ion mass peaks. For II a bond migration mechanism *via* $ClCH_2\dot{C}HCH_2Br \rightarrow ClCH_2CH{=}CH_2 + Br\cdot$ is plausible.[17] The RRKM theory predicts statistical lifetimes of $\lesssim 2 \times 10^{-12}$ sec for Br emission from the activated chlorobromoalkyl radical in both reactions I and II. The longer lifetime inferred for I thus suggests that the 1,2-chlorine migration is the rate-limiting process which makes the product angular distributions more symmetrical and the energy distributions more statistical for I than for II.

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(14) R. M. Noyes, *J. Amer. Chem. Soc.*, **70**, 2614 (1948).

(15) J. F. Harris, *J. Amer. Chem. Soc.*, **84**, 3148 (1962); F. S. Dainton and B. E. Fleischfressen, *Trans. Faraday Soc.*, **62**, 1838 (1966).

(16) A. J. Bowles, A. Hudson, and R. A. Jackson, *Chem. Phys. Lett.*, **5**, 522 (1970); A. R. Lyons and M. C. R. Symons, *J. Amer. Chem. Soc.*, **93**, 7330 (1971); T. Kawamura, D. J. Edge, and J. K. Kochi, *ibid.*, **94**, 1752 (1972).

(17) R. M. Noyes and E. Körös, *Accounts Chem. Res.*, **4**, 233 (1971), discuss isotopic labeling results for the analogous $I\cdot + CH_2{=}CHCH_2I$ reaction which are considered inconsistent with bond migration and suggest a mechanism involving halogen migration. This seems unlikely for our reaction II, however, since migration of heavy atoms prior to decomposition of the radical would be expected to provide efficient intramolecular energy exchange and thus more nearly statistical product translational distributions than observed.

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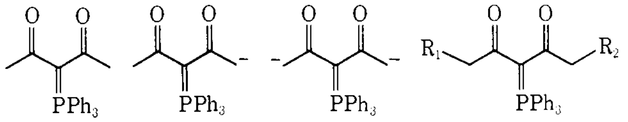
Formation of an Ylide Dianion and Its Application to the Construction of an Eight-Membered Ring

Sir:

The generation of a new anionic center adjacent to a carbonyl group already engaged in the stabilization of an existing electron donating center is a well-established phenomenon[1] and presumably reflects the ability of such a carbonyl unit to stabilize additional electronic charge. The generation of new, more reactive centers is further facilitated by the resistance of the electron-rich carbonyl group to nucleophilic attack by the highly reactive bases necessary for the formation of the new anionic center. It therefore seemed reasonable that carbonyl stabilized carbanions might also be formed in neutral systems containing a carbonyl group already engaged in charge stabilization such as found in acyl ylides, and indeed we[2] and others[3] have found that a highly reactive ylide anion is readily formed from acetylmethylenetriphenylphosphorane upon treatment with *n*-butyllithium or lithium diisopropylamide.[4]

We now wish to report the formation of both the mono- and dianion (**2** and **3**, respectively) from the diacyl ylide diacetylmethylenetriphenylphosphorane (**1**)[5] and the potential utility of dianion **3** in the construction of difficultly obtained ring systems.

Treatment of **1** with 1.2 equiv of either *n*-butyllithium or lithium diisopropylamide in THF at −78° for 5 min gives a highly colored solution containing ylide anion **2** which when treated with methyl iodide results in the formation of the substituted ylide **4**[6] (R_1 = H, R_2 = Me) in 66% yield. Likewise, treatment of **2** with *n*-propyl iodide at room temperature for 0.5 hr gives the corresponding monoalkylated ylide **4** (R_1 = H, R_2 = Pr) in good yield. Ylide anion **2** is stable at 60° for at least 10 min but is not exceptional in its nucleophilicity. Alkylation with *n*-propyl bromide gives **4** (R_1 = H, R_2 = Pr) in only 10% yield after 1 hr at room temperature and a reaction time of 10 hr is required to give a yield comparable to that obtained with *n*-propyl iodide.



1 **2** **3** **4**

Treatment of the initially formed red monoanion **2** with an additional 1.1 equiv of lithium diisopropylamide at −78° for 0.5 hr results in the formation of the black dianion **3**. Addition of excess methyl iodide to the solution containing **3** gives the dialkylated ylide **4** (R_1 = R_2 = Me) in 71% yield along with a 12% yield of monoalkylated ylide **4** (R_1 = H, R_2 = Me).[7] The increased nucleophilicity of ylide dianion **3** is evidenced by the immediate discharge of its characteristic dark color upon addition of methyl iodide at −78° while complete discharge of the lighter color characteristic of the resulting monoanion requires 0.5 hr at room temperature. Treatment of ylide dianion **3** with 1 equiv of *n*-propyl bromide at −78° for 5 min followed by quenching with water gives the substituted ylide **4** (R_1 = H, R_2 = Pr) in good yield which is in sharp contrast to the relatively slow alkylation observed with anion **2** when treated with the same reagent.

Nmr studies of acetylmethylenetriphenylphosphoranes[8] have indicated the existence of a conformational

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(1) For a recent review of the chemistry of dianions of β-dicarboxyl compounds see T. M. Harris and C. M. Harris, *Org. React.*, **17**, 155 (1969).

(2) M. P. Cooke, Jr., *J. Org. Chem.*, in press.

(3) J. D. Taylor and J. F. Wolf, *J. Chem. Soc., Chem. Commun.*, 876 (1972).

(4) A related dianion of a β-keto phosphonate has also been reported: P. A. Grieco and C. S. Pogonowski, *J. Amer. Chem. Soc.*, **95**, 3072 (1973).

(5) P. A. Chopard, R. J. G. Searle, and F. H. Devitt, *J. Org. Chem.*, **30**, 1015 (1965).

(6) Elemental analyses and spectral properties of all new compounds were in accord with assigned structures.

(7) While the formation of alkylated ylide might be explained by sequential formation of monoanions which are subsequently alkylated, we have found that treatment of **1** with 2.2 equiv of lithium diisopropylamide followed by immediate addition of excess methyl iodide gives predominantly monoalkylated ylide **4** (R_1 = H, R_2 = Me) while the dialkylated ylide **4** (R_1 = R_2 = Me) is found to be the major product when the addition of methyl iodide is delayed for 0.5 hr. The absence of 1,1-dimethylated ylide, whose formation might be expected in a scheme involving sequential anion formation, lends further support to the argument that dianion **3** is the reactive intermediate.

(8) (a) H. I. Zeliger, J. P. Snyder, and H. J. Bestman, *Tetrahedron Lett.*, 3313 (1970); (b) I. F. Wilson and J. C. Tebby, *ibid.*, 3769 (1970).