(v/v) hydrochloric acid  $(2 \times 50 \text{ mL})$  and then with saturated sodium bicarbonate solution  $(2 \times 50 \text{ mL})$ , dried (MgSO<sub>4</sub>), and concentrated to give the following: (a) The acetate (0.78 g, 2.9 m)mmol) obtained from 1 provided 0.64 g (99%) of 3,4,5-triacetoxybenzene.<sup>14</sup> (b) Similarly, the acetate (119 mg, 0.44 mmol) from 2 gave 102 mg (87%) of 3,4,5-triacetoxybenzene.<sup>14</sup> (c) The acetate (178 mg, 0.69 mmol) obtained from 4 formed 108 mg (78%) of 1,2,3-triacetoxybenzene.<sup>15</sup> (d) The acetate (106 mg, 0.54 mmol) obtained from 5 provided 78 mg (100%) of 1,2-diacetoxybenzene.<sup>16</sup> (e) The acetate (116 mg, 0.55 mmol) obtained from 7 gave 108 mg (94%) of 3,4-diacetoxytoluene.<sup>17</sup> The structures of the products were confirmed by melting point, NMR, and mass spectral analysis.

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Registry No. 1, 82280-75-9; 2, 82265-28-9; 3, 82265-29-0; 4, 82265-30-3; 5, 82265-31-4; 6, 65139-70-0; 7, 82265-32-5; 8, 82265-33-6; 9, 82265-34-7; 1,3-bis(methoxymethoxy)-5-methylbenzene, 82265-37-0; 1,3-dimethoxy-5-methylbenzene, 4179-19-5; 1,2-bis(methoxymethoxy)benzene, 3688-89-9; (methoxymethoxy)benzene, 824-91-9; benzene, 71-43-2; 1-(methoxymethoxy)-3-methylbenzene, 57234-27-2; 1-methoxynaphthalene, 2216-69-5; cuprous bromide, 7787-70-4; 4acetoxy-3,5-bis(methoxymethoxy)toluene, 82265-38-1; 4-acetoxy-3,5-dimethoxytoluene, 82265-39-2; 2,2',6,6'-tetrakis(methoxymethoxy)-4,4'-dimethyl-1,1'-biphenyl, 82265-40-5; 3-acetoxy-1,2-bis(methoxymethoxy)benzene, 82265-41-6; 2,2',3,3'-tetrakis(methoxymethoxy)-1,1'-biphenyl, 82265-42-7; 2-acetoxy-1-(methoxymethoxy)benzene, 82265-43-8; phenyl acetate, 122-79-2; 4-acetoxy-3-(methoxymethoxy)toluene, 82265-44-9; 2-acetoxy-1-methoxynaphthalene, 82265-45-0; 1-acetoxy-8-methoxynaphthalene, 82265-46-1; 8,8'-dimethoxy-1,1'-binaphthalene, 82265-47-2; [2,6-bis(methoxymethoxy)-4-methylphenyl]copper (I), 82265-35-8; bis[[2,6-bis(methoxymethoxy)-4-methylphenyl]]copper(I) lithium, 82265-36-9.

## Communications

## Transition-State Geometry in the Ene Reactions of **Mesoxalic Esters**

Summary: The evidence of a temperature-independent  $k_{\rm H}/k_{\rm D}$  value of 2.557 and a nearly identical inverse  $(k_{\rm H}/$  $k_{\rm D}$  a value of 0.950–0.957 at the  $\pi$  centers of allylbenzene strongly suggests a transition-state (TS) structure similar to that proposed for the highly reactive =S=N-. Here a symmetrically structured (2 + 2) charge-transfer complex is formed in a preliminary step, followed by a pseudopericyclic TS similar to that characterized previously<sup>21</sup> for superene reactions.

Sir: The mechanism of the ene reaction<sup>1</sup> and its broad application to organic synthesis<sup>2</sup> have been the subject of considerable study and discussion in the pages of this Journal.<sup>3-5</sup> The evidence gathered by several groups that have studied the ene reaction of dialkyl mesoxalates<sup>3-5</sup> "strongly suggest a concerted mechanism with a late product-like TS".<sup>3</sup> In this commonly held view the Htransfer step takes place in somewhat nonlinear fashion in accompaniment to nonsymmetrical breaking and formation of CH and OH bonds<sup>5</sup> (yet both steps occurring about the same time).<sup>4</sup> In other words, the classical pericyclic mechanism of this reaction discussed in reviews by Hoffmann<sup>1a</sup> and by Oppolzer and Snieckus<sup>1c</sup> is claimed to prevail in the ene reactions of mesoaxalic esters, modified by a slight deviation from linear H transfer in which the concerted transition state (TS) occurs somewhat displaced along the reaction coordinate toward the character of the product.<sup>3-5</sup> The principal purpose of the study on which





we now report was to evaluate the various views and mechanistic conclusions through the application of a mechanistic criterion more probative of TS geometry, namely, the temperature dependence of the primary kinetic deuterium isotope effect (TDKIE).

The precision of  $k_{\rm H}/k_{\rm D}$  measurement by earlier workers<sup>5</sup> apparently was not sufficient to meet the requirements for the TDKIE exercise.<sup>10</sup> In fact, the results actually obtained over a narrow (30 °C) temperature interval, with  $k_{\rm H}/k_{\rm D}$  varying from 2.36 ± 0.16 to 2.09 ± 0.13, suggested a temperature-dependent KIE, one that is normally characteristic of linear H transfer.<sup>11</sup> However, the low (average) value of  $k_{\rm H}/k_{\rm D}$  persuaded the Polish workers that they were dealing with a pericyclic TS in which there was some departure from coaxiality in the transfer of the hy-

<sup>(14)</sup> Heilbron, "Dictionary of Organic Compounds"; Oxford University Press, London, 1965.

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<sup>(11) (</sup>a) Kwart, H.; Latimore, M. C. J. Am. Chem. Soc. 1971, 93, 3770. (b) Kwart, H.; Nickle, J. H. Ibid. 1973, 95, 3394; 1974, 96, 7572; 1976, 98, 2881. (c) Kwart, H.; Sarner, S. F.; Slutsky, J. *Ibid.* 1973, 95, 5242. (d) See ref 10a. (e) Also see Drenth, W.; Kwart, H. "Kinetics Applied to Organic Reactions": Marcel Dekker: New York, 1980; Chapter 5.

## Communications



Figure 2. Pseudopericyclic course of the ene reaction of mesoxalic esters.

drogen.<sup>12</sup> Thus, following the computations of More-O'Ferrall,<sup>13</sup> calculations were carried out that purported to show that a lowering of  $k_{\rm H}/k_{\rm D}$  could correspond merely to a deviation from the pericyclic 180° angle of transfer<sup>12</sup> shown in Figure 1a. They computed that the pericyclic transition state here involved a 120° angle as shown in Figure 1b. They proposed also that the TS could include a "stabilizing" effect due to a charge-transfer interaction between the substrates", also illustrated in Figure 1b. Although a charge-transfer complex was not detected in the mesoxalic ester ene reaction, they based their proposal on the evidence of earlier authors<sup>14</sup> who reported initial color formation in the interaction of carbonyl cyanide with olefins.

In studying the TDKIE in the ene reaction between diethyl mesoxalate and allylbenzene (eq 1), it was possible



to estimate the intramolecular competition between C-H (formation of 3) and C-D (formation of 4) bond breaking through the use of the <sup>2</sup>H NMR probe in a 250-MHz FT instrument equipped with a calibrated electronic integrator. The high precision inherent in this method of measurement of the KIE has previously been established.<sup>15</sup> The results of such measurements, averaging more than 1000 scans in each case, with determinations made over an 80 °C temperature range, are listed in Table I.

Table I. Temperature Dependence of the Primary Deuterium Isotope Effect<sup>a</sup> in the Ene Reaction of  $C_{c}H_{c}CHDCH=CH_{2}$  with Diethyl Mesoxalate (1)

<i>T</i> , °C (±0.05 °C)	$(k_{\rm H}/k_{\rm D})^{b}$	mean $(k_{\rm H}/k_{\rm D})^b$ in $\Delta T = 80 ^{\circ}{\rm C}$
200.0 180.0 160.0 140.0	$\begin{array}{r} 2.575 \pm 0.015 \\ 2.574 \pm 0.015 \\ 2.546 \pm 0.015 \\ 2.545 \pm 0.015 \end{array}$	$2.56 \pm 0.01;$ SD = 0.016; variance = $1.91 \times 10^{-4}$
120.0	$2.548 \pm 0.015$	

<sup>a</sup> Kinetic procedure: An NMR tube was charged with 450 mg (253 mmol) of diethyl mesoxalate and 300 mg (254 mmol) of the deuterated allylbenzene in 500 mg of very dry solvent diglyme. The tube was cooled to -78 °C and degassed in a series of freezing-pumping-thawing cycles before sealing. It was then inserted into the thermostated bath and held there until the reaction was complete as determined by an NMR procedure in a preliminary undeuterated run. The tube was then removed from the bath, cooled, and inserted in the <sup>2</sup>H NMR probe of a 250-MHz FT instrument for measurement of the integrated intensities of the two lines corresponding to 3 (the C-D line) and 4 (the O-D line), respectively. Repeated evaluations on a given sample always yielded nearly identical values of the isotope ratio, which will be seen to be equal to  $k_{\rm H}/k_{\rm D}$ . <sup>b</sup> Precision: In the closed system described in the kinetic procedure (above), only the deuterated products and reactants are visible to the <sup>2</sup>H NMR probe. Thus, it is possible to readily establish the three criteria on which the precision of the measurements depend: (i) all the starting material containing deuterium has been reacted, (ii) the starting material is sufficiently pure and contains no 3-phenylpropene- $3,3-d_2$ , and (iii) no significant loss of D on oxygen through NMR-detectable exchange with any component of the medium has occurred.

The value of  $k_{\rm H}/k_{\rm D}$  is found to be temperature independent,<sup>16</sup> i.e.,  $k_{\rm H}/k_{\rm D} = A_{\rm H}/A_{\rm D}$ ; moreover,  $A_{\rm H}/A_{\rm D} \gg \sqrt{2}$ , the maximum value expected for a linear H-transfer TS. These data represent the strong indication that the TS of the ene reaction here is a bent one. Since nonlinear H transfer is clearly not in keeping with the classical pericyclic TS of an ene reaction,<sup>1</sup> a rather drastic modification of the currently accepted mechanism<sup>3-5</sup> of this reaction is required.

As in the cases of nonlinear allylic H-abstraction processes previously identified,<sup>16a</sup> consideration was given to the possibility that a rapidly reversible, preliminary com-

<sup>(12)</sup> The fallacy of the widely held view that low values of  $k_{\rm H}/k_{\rm D}$ invariably signify a bent TS (for examples see ref 13, as well as Dai, S.-H.; Dolbier, H. R., Jr. J. Am. Chem. Soc. 1972, 94, 3953, and Saunders, W. J., Jr. Chem. Scr. 1976, 10, 82; 1975, 8, 27) has recently been discussed in a forthcoming publication by H. Kwart, M. W. Brechbiel, R. M. Acheson, D. C. Ward, wherein values of  $k_{\rm H}/k_{\rm D}$  as large as 5.1 at temperatures in the region of 150 °C are found for reactions unequivocally characterized by a bent TS.

 <sup>(13)</sup> More-O'Ferrall, R. A.; Kouba, J. J. Chem. Soc. B. 1967, 965.
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<sup>18, 31.</sup> Also see Chem. Abstr. 1970, 72, 120984g.

<sup>(15)</sup> Kwart, H.; Benko, D. A.; Streith, J.; Harris, D. J.; Schuppiser, J. L. J. Am. Chem. Soc. 1978, 100, 6501.

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Table II. Secondary Deuterium Isotope Effects<sup>*a*</sup> in the Ene Reaction of 3-Phenylpropene and Diethyl Mesoxalate (1) at 180  $\pm$  0.05 °C

position of deuteration in 3-phenylpropene	f <sup>b</sup>	$R_{A_f}{}^b$	$R_{A_0}{}^b$	$[(k_{\rm H}/k_{\rm D})\alpha]/{\rm D}$	av $(k_{\rm H}/k_{\rm D}) \alpha$
 C <sub>2</sub> (1 D)	0.837	2.3521		0.951	0.957 ± 0.006
C <sub>2</sub> (2 D)	0.829	2.3557		0.964	
C <sub>1</sub> (2 D)	0.852	1.2237		$(0.9017)^{1/2} = 0.950$	$0.950 \pm 0.001$
C <sub>1</sub> (2 D)	0.897	1.2100	(0.9050)	$(0.9050)^{1/2} = 0.951$	
$C_{2}(1 D)$	0.00		2.3099		
<b>C</b> <sub>1</sub> (2 <b>D</b> )	0.00		1,1818		

<sup>a</sup> Kinetic procedure: The respective mono- and dideuterated allylbenzenes<sup>17</sup> were added together with protioallylbenzene to obtain a ca. 50:50 mixture. A Pyrex reaction tube was charged with this mixture and the equivalent amount of diethyl mesoxalate and solvent as described in the procedure of Table I. After sealing of the tubes and immersion in the thermostat, an appropriate interval of reaction time was allowed (as previously determined) to effect the desired degree of completion. The vials were then rapidly cooled and opened. The contents were poured into water and extracted with pentane. The neutral extracts were combined, dried over MgSO<sub>4</sub>, and carefully concentrated. The residue was checked on a precision GLC instrument for degree of conversion relative to an internal standard. The remainder of the solution was preparative gas chromatographed on a 0.25 in.  $\times 4$  ft, 10% SE-30 column, condensing the allylbenzene fraction in a dry capillary at -78 °C. Analysis of the appropriate mass ratios was performed by the MS technique previously described,<sup>10</sup> using the required correction factors also discussed in these references. <sup>b</sup> Computations: The values of  $k_{\rm H}/k_{\rm D}$  were calculated with the aid of the equation,  $1/(k_{\rm H}/k_{\rm D}) = \{[\ln (R_{\rm A_f}/R_{\rm A_0})]/[\ln [(1-f)(1+R_{\rm A_0})/(1+R_{\rm A_f})] + 1\}$ , where  $R_{\rm A_0}$  is the ratio of heavy to light isotope MW at t = 0 and  $R_{\rm A_f}$  is the heavy to light ratio after an f fraction of reaction is completed.

plex of the ene and enophile was formed in low concentrations prior to the rate-determining H transfer, a situation which is still in accord with the kinetics. To probe for the intervention of a CT complex along the pathway to product, rather than some rapidly reversible, colored, side-reaction product (as could be the case in the carbonyl cyanide ene reaction<sup>14</sup> cited<sup>5</sup> above), we devised a secondary D isotope effect test. The results listed in Table II show that inverse secondary D isotope effects of almost identical magnitude exist at both ends of the double bond. They comprise the most definitive evidence for a symmetrically structured intermediate lying close to the major TS of this ene reaction.

Furthermore, in previously studied cases of an allylic H-abstraction TS, where a bridged radical complex has been implicated,<sup>17</sup> as well as in a variety of bridged intermediates shown to be formed in the course of addition reactions of the double bond,<sup>18</sup> the inverse secondary D isotope effects are found to be different at both ends of the double bond. This has been interpreted<sup>18</sup> as descriptive of the dissymmetry of the three-membered-ring,  $\pi$ -type complex. By contrast a (2 + 2) cyclic complex possessing a symmetrical interaction structure might be deduced here from the very symmetry of the inverse secondary isotope effect results.

A second feature of the highly electrophilic heteroenophile that greatly beneficiates this ene reaction process stems from the presence of an n electron pair. The participation of such properly oriented, unshared electrons of a member atom of the complex is what brings about the angular H abstraction in the course of exchanging roles with a bonding electron pair in the pseudopericyclic<sup>19</sup> TS. A fruitful analogy is to the superenophilic reagents ArN=S=X (for example, where Ar = tosyl and X = O) of Kresze and co-workers.<sup>20</sup> Evidence has been presented to support the proposal that a super-ene reaction involves a bent TS of nonlinear H transfer arising from a fourmembered complex of the reactants in which the unshared pair on nitrogen becomes the agent of H abstraction in the "pseudopericyclic" process.<sup>21</sup> A somewhat analogous picture of the course of the ene reaction between mesoxalic esters and allylic olefins, illustrated in Figure 2, is regarded as completely in accord with the results being reported here.

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Registry No. Diethyl mesoxalate, 609-09-6; allylbenzene, 300-57-2; deuterium, 7782-39-0.

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## Sulfur-33 Nuclear Magnetic Resonance Spectroscopy of Simple Sulfones. Alkyl-Substituent-Induced Chemical Shift Effects

Summary: The <sup>33</sup>S NMR chemical shifts of a series of symmetrical dialkyl and diaryl sulfones as well as some cyclic sulfones have been measured and the magnitude of the  $\beta$ -methyl substituent effect has been determined. The <sup>33</sup>S nuclei of diaryl sulfones are more shielded than the dialkyl sulfones and diastereoisomeric sulfones are distinguishable.

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