

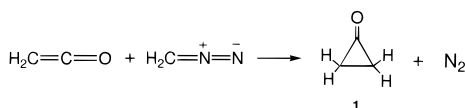
An Oxyallyl (or Oxyallyl-like) Geometry Is a Key Structure in the Reaction of Ketenes and Diazoalkanes To Form Cyclopropanones

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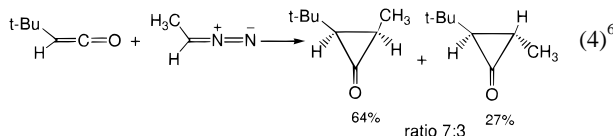
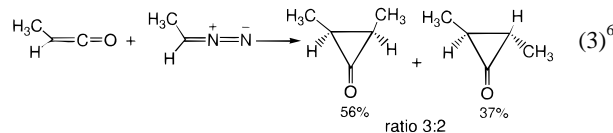
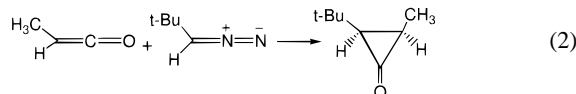
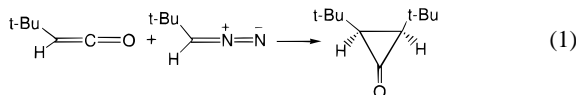
Cyclopropanone (**1**)¹ was first prepared by the thermal reaction of ketene with diazomethane, and substituted derivatives have been prepared² by the reactions of substituted ketenes and diazomethanes. Turro and Hammond³ have speculated on possible reaction mechanisms, but as noted recently by Berson,⁴ “the mechanism of diazomethane’s addition to ketenes is not known”.



In the present study, which is directed toward this deficiency, we have used an interplay of experimental and theoretical chemistry to interpret the basic stereochemical features of this reaction, i.e., using alkyl substituted ketenes and diazoalkanes as starting materials.

The following experimental results are notable (all reactions were initially carried out at -78°C in CD_2Cl_2 solvent and examined *in situ* by ^1H and ^{13}C NMR spectroscopy, eqs 1–4).⁵

Several conclusions can be drawn from these results: (1) The



cyclopropanone stereochemistry does not appreciably depend on the size of the alkyl group of the ketene (cf., eq 1 *vs* 2 or eq 3 *vs* 4). (2) Conversely, the stereochemical result is quite

(1) (a) Lipp, P.; Buchkremer, J.; Seeles, H. *Ann. Chem.* **1932**, 499, 1. (b) Semenow, D. A.; Cox, E. F.; Roberts, J. D. *J. Am. Chem. Soc.* **1956**, 78, 3321. (c) Kende, A. Ph.D. Dissertation, Harvard University, **1956**. (d) Turro, N. J.; Hammond, W. B. *J. Am. Chem. Soc.* **1966**, 88, 3672. (e) Schaafsma, S. E.; Steinberg, H.; de Boer, T. *J. Recl. Trav. Chim. Pays-Bas* **1966**, 85, 1170. (f) Rodriguez, H. J.; Chang, J.-C.; Thomas, T. F. *J. Am. Chem. Soc.* **1976**, 98, 2027.

(2) For a review, see: Turro, N. *J. Acc. Chem. Res.* **1969**, 2, 25.

(3) Turro, N. J.; Hammond, W. B. *Tetrahedron* **1968**, 24, 6017. See also: Kende, A. *Chem. Ind.* **1956**, 1053.

(4) Cordes, M. H. J.; Berson, J. A. *J. Am. Chem. Soc.* **1996**, 118, 6241.

(5) Only *cis*-2,3-di-*tert*-butylcyclopropanone has been reported: Sorensen, T. S.; Sun, F. *J. Am. Chem. Soc.* **1995**, 117, 5592; *Can. J. Chem.* **1997**, 75, 1030. However, the other *cis*- and *trans*-dialkylcyclopropanones are distinguished by the H2–H3 coupling constant: 17–18 Hz for *cis*, 7–9 Hz for *trans*.

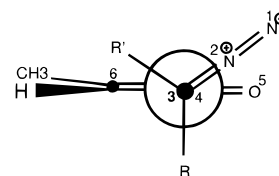


Figure 1. Expected direction of the initial attack by a diazoalkane carbon on the carbonyl carbon of a ketene. There are various possible rotamers about the forming C3–C4 “bond” but the orientation shown is approximately that found for **TS1A** ($\text{R} = \text{CH}_3$, $\text{R}' = \text{H}$) in Figure 2.

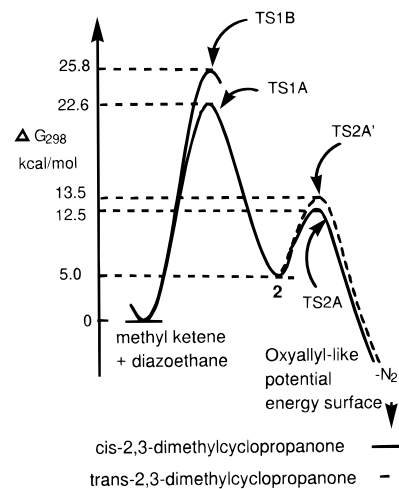


Figure 2. Calculated (B3LYP/6-31G*) free energy diagram of the reactants, intermediate **2**, and transition states for the methyl ketene–diazoethane reaction. **TS1B** also leads to an intermediate isomeric with **2**, but this path is not expected to be operative and is not shown.

dependent on the size of the alkyl group of the diazoalkane (cf., eq 1 *vs* 4 or eq 2 *vs* 3). (3) The exclusive *cis*-cyclopropanone stereochemistry in eqs 1 and 2 (particularly eq 1) is an indication that strong stereoelectronic factors are involved in the cyclopropanone formation since *cis*-2,3-di-*tert*-butylcyclopropanone has been computed to be 7.21 kcal/mol less stable than the corresponding *trans* isomer.⁵

A ketene is known to undergo nucleophilic attack at the carbon of the carbonyl (the π -type LUMO of a ketene has a large carbonyl carbon coefficient),⁷ but because of the allenic bonding of a ketene, the nucleophile (in our case diazoalkane) is required to approach this π -orbital in the same plane as that containing the ketene substituent groups. The π -type HOMO orbital of a diazoalkane constitutes an ambident nucleophile, with large coefficients (antiphase) on both C and terminal N. For carbon as the nucleophile in the diazoalkane, initial orbital overlap with a ketene is expected along the axis of this C π -orbital, and one can use a Newman projection (Figure 1), sighting along the newly forming bond, to visualize the overall geometry (with various rotamers possible).

Molecular orbital (MO) calculations^{8,9} were undertaken concurrently with the experimental work. Results for the diazoethane–methyl ketene reaction (B3LYP/6-31G* level) are illustrated in Figure 2 and can be summarized: (1) Transition-states **TS1A** and **TS1B** (Figure 2) were located for the rate-determining attack of diazoethane on the H or CH_3 side of methyl ketene. These resemble the Figure 1 structure (ketene

(6) In eq 3, a third product (7%) is also formed, and in eq 4, one also sees a third product (9%). These are tentatively assigned to allene oxide structures.

(7) Tidwell, T. T. *Ketenes*; John Wiley and Sons, Inc.: New York, 1995.

(8) Some ketene reactions have previously been modeled by MO methods, e.g.: see Sordo, J. A.; González, J.; Sordo, T. L. *J. Am. Chem. Soc.* **1992**, 114, 6249.

(9) Gaussian 94, (Revision A.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

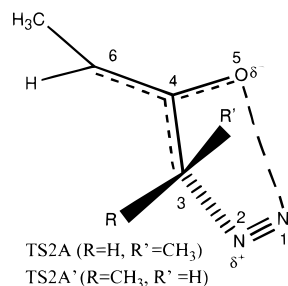
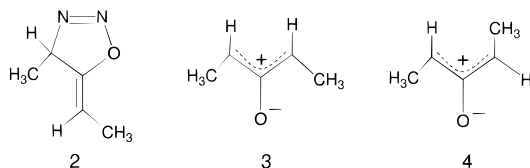


Figure 3. Approximate structure of **TS2A** and **TS2A'** transition states. As N_2 “departs” in the continuing reaction, bonds C4–C6 and C3–C4 become nearly equal, R' occupies a position *syn* to oxygen, R occupies an *anti* position, R , and C6 begins to twist in a disrotatory manner with respect to the twist already present at C3.

H and CH_3 interchanged for **TS1B**), with a long C3–C4 bond (1.96–1.97 Å) and a N2–C3–C4–O5 dihedral angle of *ca.* 20°. (2) The CH_3 group of diazoethane in **TS1A** is located in the R position, and attempts to locate another transition state where H and CH_3 were interchanged led to the same result. (3) Transition-state **1B** is 3.16 kcal/mol higher in energy than **1A**, because of steric interactions between ketene CH_3 and diazoethane H. (4) The cyclic intermediate from **TS1A**, structure **2**,¹⁰ can lose N_2 via two different second transition states, labeled **2A** and **2A'**, whose structures are sketched in Figure 3. These transition states differ in energy by only 1.02 kcal/mol, because C4 is fully sp^2 -hybridized, moving the CH_3 of the diazoethane away from the ketene H and lessening the steric differentiation. In **TS2A** and **TS2A'**, the C3–C4 bond is short (1.49 and 1.50 Å, respectively) and C3–N2 is long (1.70 and 1.77 Å). IRC (intrinsic reaction coordinate) calculations show that **TS2A** leads to *cis*-2,3-dimethylcyclopropanone and **TS2A'** to the *trans* isomer.¹¹ As N_2 leaves from **TS2A**, a *syn, syn*-dimethyloxyallyl-like structure (**3**) results and then this undergoes disrotatory closure.¹² In the **TS2A'** case, a *syn, anti*-dimethyloxyallyl-like structure (**4**) is involved.



With methyl ketene, the side selectivity of the diazoethane attack (calculated $\Delta\Delta G^\ddagger$ difference of 3.2 kcal/mol) sets up a *syn* orientation at one center of the developing oxyallyl-like

(10) **TS1A** was also obtained using a solvation (acetonitrile) simulation procedure (SCI-PCM Model User's Reference, Gaussian 94, Gaussian Inc., Pittsburgh, PA, 1995, p 151 and refs 155–157). The C3–C4 bond is longer (2.08 Å), but the dihedral N2–C3–C4–O5 angle is smaller (15.2°) than in the gas-phase result. Optimization from solvated **TS1A** gives solvated **2**. The ΔE^\ddagger from **2** is reduced from 21.5 kcal/mol (gas phase) to 18.5 kcal/mol. Since CH_3CN is more polar than CH_2Cl_2 , we conclude that solvation effects do not change the nature of **TS1**.

(11) The IRC calculation was allowed to proceed to the van der Waals separation distance for N_2 and the organic fragment, *ca.* 3 Å. Optimization of the organic fragment was then carried out from this point.

structure, and we postulate that this center will be exclusively *syn* for any monoalkyl ketene. The secondary transition-states **2A** and **2A'** set up the second geometric center, and we postulate that these are similar enough in energy in the diazoethane case that a mixture of both *syn* and *anti* geometries result. However, with large R groups in the diazoalkane (*tert*-butyl), molecular modeling studies show that **TS2A** ($R' = t\text{-Bu}$) will be strongly preferred over **TS2A'** ($R = t\text{-Bu}$).

One can now interpret the eqs 1–4 results from this basic model. As stated, we assume that all diazoalkanes attack the H side of a monoalkyl ketene; thus methyl and *tert*-butyl ketenes give qualitatively similar results (eq 1 *vs* 2 and eq 3 *vs* 4). In both cases, the ketene alkyl group will occupy a *syn* orientation in the developing oxyallyl structure. With a large R group on the diazoalkane (*tert*-butyl), **TS2A** will be preferred over **2A'**, thereby also leading to a *syn* orientation for this group and *cis* stereochemistry in the cyclopropanones (eqs 1 and 2). With a small R group, both transition-states **2A** and **2A'** are involved and both *cis* and *trans* cyclopropanones are formed (eqs 3 and 4).

For the diazomethane–ketene calculations, we also find **TS1** and **TS2** and an intermediate related to **2**.¹³ From **TS2** to cyclopropanone, the IRC follows a potential energy surface in which the organic fragment is oxyallyl-like in structure, although the reaction is more concerted than in the dimethyl case.¹⁴ We believe that these experimental and theoretical results strongly corroborate each other and clearly implicate an oxyallyl (or oxyallyl-like) structure in the formation of cyclopropanones from diazoalkanes and ketenes.

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Supporting Information Available: Low-temperature NMR spectra of eqs 2–4 involving the previously uncharacterized cyclopropanones; coordinates and energies for **TS1A**, **TS1B**, **TS2A**, **TS2A'**, **2**, diazoethane, methyl ketene, and *cis*- and *trans*-2,3-dimethylcyclopropanone; plot of the oxyallyl-like structures obtained from IRC calculations (15 pages). See any current masthead page for ordering and Internet access instructions.

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(12) Oxyallyls have been computed as minima using CASSCF methods, see: Lim, D.; Hrovat, D. A.; Borden, W. T.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1994**, *116*, 3494. The calculated transition state for disrotatory ring-closure of oxyallyl to cyclopropanone is very small and the geometry resembles oxyallyl (24° twist of terminal carbons). At the B3LYP/6-31G* level, we do not locate minima for either *syn–syn* or *syn–anti* dimethyloxyallyl. Therefore, in our IRC calculations, we would obviously not expect to find an oxyallyl intermediate. As N_2 leaves in the IRC sequence, one can describe the other fragment as an “oxyallyl-like” structure (see the Supporting Information); the main difference between this geometry and a planar oxyallyl is a twist of the terminal carbons. However, the *syn–anti* stereochemical feature of an oxyallyl is present and the disrotatory motion of the above twist is also inherent in the somewhat concerted movement of atoms as N_2 leaves. It is possible that other levels of theory will find an oxyallyl minimum in the IRC sequence, but this would not change the essence of the stereochemical features of the present mechanism.

(13) Summary energies: **TS1**, 23.4; intermediate related to **2**, 7.5; **TS2**, 18.9, all $\Delta\Delta G_{298}^\ddagger$ kcal/mol above a zero reference for diazomethane plus ketene.

(14) Where C–N = 2.06 Å, the “oxyallyl” C1–C3 distance is still 2.21 Å, but for C–N = 2.44 Å, C1–C3 is only 1.94 Å. For C–N = 2.90 Å, C1–C3 = 1.57 Å, i.e., cyclopropanone is nearly completely formed.