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Theoretical Studies of the Structures and Reactions of Substituted Carbonyl Ylides

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Abstract: The electronic structures and geometries of model substituted carbonyl ylides containing amino, cyano, and phenyl substituents were investigated by ab initio SCF calculations using the STO-3G and 4-31G basis sets and 3 × 3 CI. Stabilization and geometrical distortions caused by substituents, barriers to isomerization, the ease of formation of carbonyl ylides from oxiranes, the regioselectivity of fragmentations of carbonyl ylides, and the regioselectivities and reactivities of cycloadditions of substituted carbonyl ylides were investigated.

Introduction

In 1965, Linn and Benson discovered that tetracyanoethylene oxide undergoes cycloadditions to alkenes across the CC single bond. Kinetic studies implicated the formation of a reactive intermediate, now known definitely to be a carbonyl ylide.[2] Earlier, Ullman and Milks observed the formation of relatively stable cyclic carbonyl ylides upon thermolysis, or photolysis, of an indenone oxide.[3] In 1967, Griffin and coworkers discovered the photochemical fragmentation of oxiranes,[4] and later showed that carbonyl ylides were detectable intermediates upon photolysis of oxiranes in low-temperature glass matrices.[5,6] Huisgen and co-workers studied the thermal cycloadditions of oxiranes, and proved beyond doubt that carbonyl ylides are intermediates in these reactions.[7] The chemistry of substituted carbonyl ylides is summarized in Figure 1.

Several theoretical studies of the parent carbonyl ylide (2-oxatrimethylene) and its formation from oxirane have been reported, and during the course of our work Bigot, Sevin, and Devaquet reported high-level ab initio calculations on the parent oxirane–carbonyl ylide interconversion and the fragmentation of oxirane and carbonyl ylide to carbonyl and carbene fragments.[8,9] Our investigation forms a natural complement to the reports by these authors, since we have concentrated on the influence of substituents on energies of the various species and processes shown in Figure 1.

In this paper, we attempt to establish a number of details about carbonyl ylides which only can be indirectly inferred from experiment. In particular, using ab initio SCF calculations[10] with the STO-3G[11] and 4-31G[12] basis sets, and 3 × 3 CI,[13] we have attempted to answer the following questions: (1) How do substituents facilitate the thermal ring opening? (2) How do substituents influence the geometries and the barriers to isomerization of carbonyl ylides? (3) How do substituents influence the reactivities and regioselectivities of carbonyl ylides in cycloaddition reactions? (4) Are fragmentations of substituted carbonyl ylides thermal or photochemical processes? (5) What controls the direction of the fragmentation?

Molecular Orbitals of Carbonyl Ylide. The high-lying filled and low-lying vacant molecular orbitals of the parent carbonyl ylide primarily located on heavy atoms are shown in Figure 2. In addition to the familiar allyl-anion-like π molecular orbitals, π_1, π_2, and $\pi_3{}^*$, the valence orbitals of the heavy-atom skeleton of the planar molecule include filled oxygen lone-pair and CO bonding orbitals, as well as vacant CO antibonding orbitals. The last two appear as combinations which are symmetry adapted with respect to the symmetry plane bisecting the molecule. In our discussion, we will describe the planar geometry as the 0°,0° conformation, following Hoffmann's nomenclature.

Upon a 90° rotation of one CH_2 to form the 0°,90° conformation, π_1, π_2, and $\pi_3{}^*$ correlate with the π_{CO}, the carbon lone pair (n_C), and π^*_{CO} orbitals, respectively, while double rotation to the 90°,90° geometry gives two carbon lone pairs and the out-of-plane oxygen long pair. However, since the highest occupied molecular orbital (HOMO) and the lowest unoccupied MO (LUMO) are close in energy, the molecule may have appreciable diradical character. That is, it may prove necessary to describe this molecule as a linear combination of the ground configuration shown ($\ldots \pi_2{}^2\pi_3{}^{*0}$) and a doubly excited configuration ($\ldots \pi_2{}^0\pi_3{}^{*2}$).

Whereas a closed-shell description of a diradical species overestimates the zwitterionic character of the wave function, a linear combination of the ground and double excited configurations eliminates much of this zwitterionic character.[14] Hayes and Siu carried out 2 × 2 configuration interaction calculations on the parent carbonyl ylide and found that the ground state was composed of 81% of the ground configuration and 19% of the doubly excited configuration.[15] They described carbonyl ylide as a molecule with 38% (=2 × 19%) diradical

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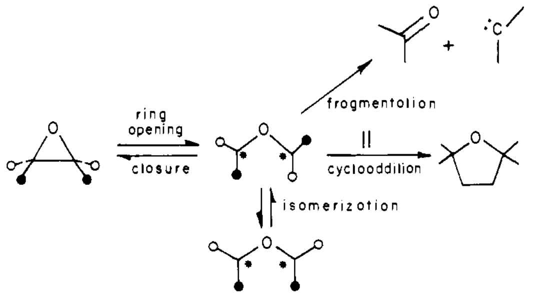


Figure 1. Summary of the chemistry of carbonyl ylides.

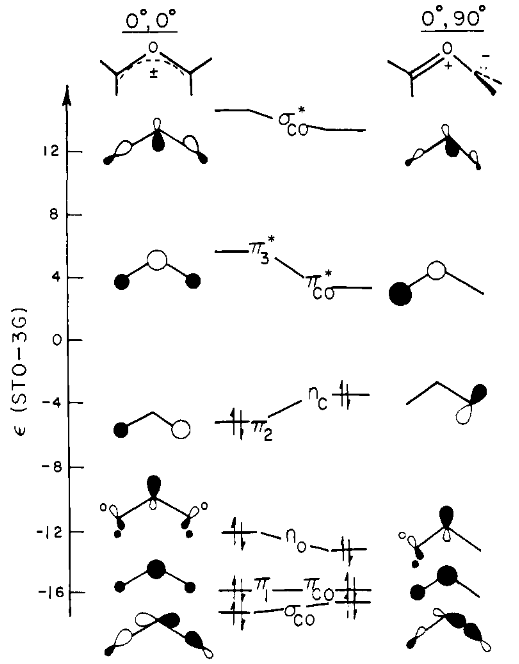


Figure 2. Geometrical definitions and orbitals involving predominantly heavy atoms in carbonyl ylide.

character. Similar calculations indicate that trimethylene has 80% diradical character.[15]

Hayes also investigated the relative energies of 0°,0° and 90°,90° geometries for various COC angles. The former was an energy minimum at 130°, and latter at 60°, essentially at the oxirane geometry.[16] Devaquet and co-workers reported two standard geometries for carbonyl ylide: the 90°,90° (face-to-face) species was found not to be energy minimum relative to oxirane, and was 18 kcal/mol higher in energy than the 0°,0° (edge-to-edge) species.[8]

The geometry of carbonyl ylide previously has been optimized by us, using MINDO/2 and MINDO/3,[17] by Leroy and co-workers using STO-3G,[18] and by Yamaguchi and co-workers using an unrestricted MINDO/3 method (UMINDO/3).[19] The results of these calculations are shown in Figure 3. Yamaguchi and co-workers also found that carbonyl ylide is "triplet unstable", that is, that a single configuration is insufficient to adequately describe the ground state of this species, so that unrestricted HF calculations are required.[20] These authors also described carbonyl ylide as significantly diradical in character, but showed that substituted ylides such as the tetracyano derivative are more accurately described as closed-shell zwitterions.[19,20]

Hiberty and Leforestier optimized the CO bond lengths for a planar structure of carbonyl ylide, fixing r_{CH} at 1.08 Å and all angles at 120°, using the STO-3G basis and 6 × 6 CI.[21] The optimum value found for r_{CO} was 1.342 Å. These authors also evaluated the weights of various valence-bond structures contributing to the ground state, and found that the diradical

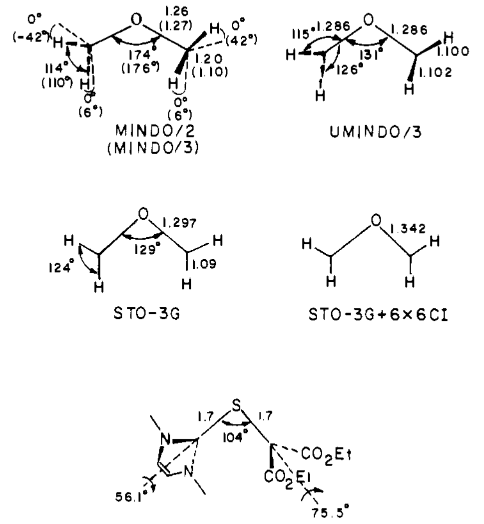


Figure 3. Previously reported geometries of carbonyl ylide and a thiocarbonyl ylide.

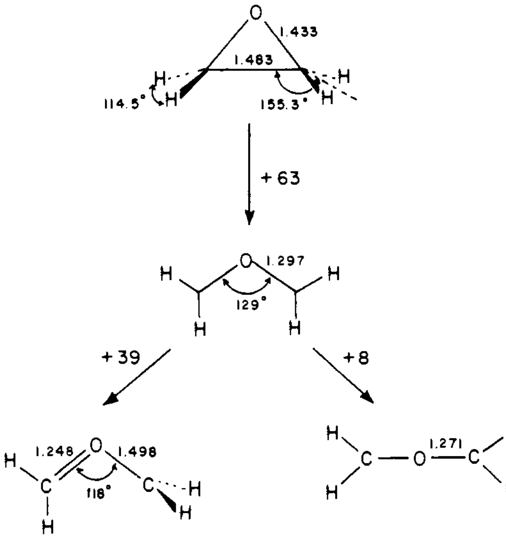


Figure 4. Relative energies (4-31G) of various carbonyl ylide geometries.

VB structure, $\dot{C}$—O—$\dot{C}$, is 55% of the ground-state wave function, while zwitterionic structures, C^{-}—O^{+}=C and C^{-}—O—C^{+}, and the oppositely polarized ones, constitute 42% of the ground-state wave function. A single determinant ground configuration, as expected, overestimates the zwitterionic character of these species, indicating only 24% diradical and 67% of the aforementioned zwitterionic character.[21]

Finally, Arduengo and Burgess have optimized, by MINDO/3, and have determined, by X-ray crystallography, the structure of the substituted thione methylide (thiocarbonyl ylide), shown at the bottom of Figure 3.[22] This species favors a nonplanar geometry with both termini rotated out of planarity by the amount shown.[22]

Geometry, Energy, and Isomerization Pathways of Carbonyl Ylide

An optimization of the geometry of carbonyl ylide at the STO-3G level gives the geometry shown in the center of Figure 4.[18,23] The STO-3G geometry of oxirane has been published.[24] For the remaining species which we investigated, the CH bond lengths were fixed at 1.09 Å and the HCO angles at 118° (∠HCH = 124°), while the COC bond lengths and angle were optimized at the STO-3G level. Although the use of single-determinant calculations on species having appreciable di-

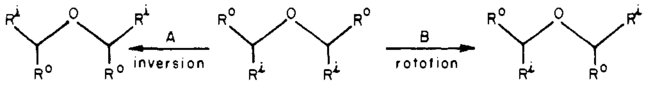


Figure 5. Types of isomerization of carbonyl ylides.

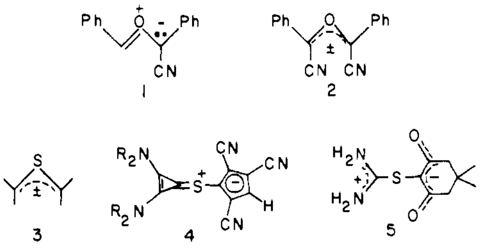


Figure 6. Push-pull substituted systems.

radical character is open to criticism, the 4-31G calculations given in Figure 4 are in reasonable agreement with the calculations using extensive CI reported by Devaquet et al.[8,9] These authors report that the 0°,0° carbonyl ylide is 65 kcal/mol higher in energy than oxirane (cf. 63 by 4-31G), and that the 90°,90° carbonyl ylide is 83 kcal/mol above oxirane. Both 4-31G and Devaquet's STO-3G CI calculations indicate that the 90°,90° form is not an energy minimum.

The CO bond length (1.297 Å) of planar carbonyl ylide is intermediate between the double bond of formaldehyde (1.119 Å)[25] and the single bond of dimethyl ether (1.416 Å),[25] although the more extensive calculations by Hiberty suggest a CO bond length nearer that of dimethyl ether.

An upper limit to the enthalpy of CC ring opening of oxirane can be estimated from the experimental heats of formation of ethylene oxide (−12.6 kcal/mol)[27a] and dimethyl ether (−44.0 kcal/mol)[27a] and from the bond dissociation energy of a CH bond in dimethyl ether (93.3 kcal/mol).[28] Assuming that removal of each hydrogen from the methyls requires 93.3 kcal/mol, the estimated heat of formation of $\cdot CH_2OCH_2\cdot$ is +38.4 kcal/mol, using 52.1 kcal/mol for $\Delta H_f°$ (H·). This value is an average of the energies of the singlet and triplet species, and furthermore assumes no stabilizing interaction between the odd electrons.[27b] This estimate gives +51 kcal/mol as the energy of CC cleavage in oxirane, reasonably close to the 4-31G theoretical value. Similar estimates for CO cleavage give an estimate of +54 kcal/mol for this reaction.

Rotation about one CO bond of carbonyl ylide is energetically costly, and gives a species with substantially more zwitterionic character than the 0°,0° form, as reflected by the increase in calculated dipole moment described later. Upon rotation, the "carbonyl" bond becomes only 0.13 Å longer than the experimental bond length of formaldehyde, while the single bond stretches to a value of 0.07 Å larger than the experimental CO length of dimethyl ether. The HOMO is essentially a lone pair on the 90° rotated methylene, while the LUMO is essentially a π^*_{CO} orbital of the planar fragment.

The total charge on the 90° methylene is only −0.36, since there is considerable reorganization of the σ orbitals to compensate for the charge separation. The 0° methylene has a charge of +0.18 in this structure. It is likely that the carbanion-like terminus will pyramidalize, although our calculations did not permit this geometrical relaxation. Calculations on carbonyl oxide (which is more like the unsymmetrically substituted cases discussed below) give barriers to CH_2 rotation of 29.1[29] and 12.4 kcal/mol.[30]

Inversion of oxygen occurs with only small barriers in all of the calculations. This suggests that the inversional isomerization of appropriately substituted carbonyl ylides will be substantially easier than rotational isomerization (Figure 5). This is even more impressive since the "inversion" of water is calculated to have a barrier of 26 kcal/mol at the optimized 4-31G level.

In summary, the parent carbonyl ylide is predicted to be a planar species which will rapidly invert about oxygen but only slowly rotate about the partial CO double bond. Both the substantial barrier to pyramidalization of CH_2's and the sizable barrier to CO rotation suggest that carbonyl ylide is a considerably delocalized species. We emphasize the qualitative nature of these numerical estimates, but in light of favorable comparisons with extensive CI calculations the qualitative conclusions appear secure.

Geometries and Energies of Substituted Carbonyl Ylides

Calculations have been carried out on a number of model substituted carbonyl ylides. For most of these studies, extremes of donor and acceptor substitution were simulated by the use of standard amino and cyano groups, respectively.[31] Only the CO lengths and COC angles were optimized at the STO-3G level. The energies of these species will be discussed first, and then the geometries and barriers to rotation will be compared to the parent species.

"Push-Pull" Stabilization of Carbonyl Ylides. Organic chemists have developed a rule of thumb that substitution of donors and acceptors on opposite sides of reactive intermediates containing delocalized π systems causes stabilization. In the carbonyl ylides, this is manifested in the relative ease of thermal generation of species such as **1** and **2** shown in Figure 6,[7] while normally transient thiocarbonyl ylides, **3**, can be made isolable by the extremes of donor and acceptor substitution present in the stable molecules, **4** and **5**.[32] In valence-bond terms, such substitution mixes structures such as those shown in **1**, **2**, **4**, and **5** into those also present in the parent species. However, addition of such resonance structures is not in itself sufficient to provide stabilization. For example, Hoffmann has provided an MO explanation for the stability of push-pull stabilized cyclobutadiene when donors are located diagonally, but not laterally, even though equally attractive resonance structures can be drawn for both.[33]

For the carbonyl ylides, computational estimates of the magnitude of stabilization by donors (amino groups) and acceptors (cyano groups) and by push-pull substitution are described first, followed by a rationalization of these results.

Energies of isodesmic reactions, calculated by STO-3G, are shown in the equations below. The stabilization energies calculated relative to the parent ylide are summarized in Figure 7.

$$CH_2OCH_2 + CH_3NH_2 \rightarrow NH_2CHOCH_2 + CH_4 \quad -5\ \text{kcal/mol} \quad (1)$$

$$CH_2OCH_2 + CH_3CN \rightarrow CH_2OCHCN + CH_4 \quad -16\ \text{kcal/mol} \quad (2)$$

$$CH_2OCH_2 + 2CH_3CN \rightarrow NCCHOCHCN + 2CH_4 \quad -25\ \text{kcal/mol} \quad (3)$$

$$CH_2OCH_2 + 2CH_3CN \rightarrow CH_2OC(CN)_2 + 2CH_4 \quad -28\ \text{kcal/mol} \quad (4)$$

$$CH_2OCH_2 + CH_3CN \rightarrow H_2NCHOCHCN + 2CH_4 + CH_3NH_2 \quad -33\ \text{kcal/mol} \quad (5)$$

$$CH_2OCH_2 + CH_3CN \rightarrow CH_2OC(NH_2)(CN) + 2CH_4 + CH_3NH_2 \quad -17\ \text{kcal/mol} \quad (6)$$

$$CH_2OCH_2 + 2CH_3NH_2 \rightarrow (NH_2)_2COC(CN)_2 + 4CH_4 + 2CH_3CN \quad -76\ \text{kcal/mol} \quad (7)$$

$$CH_2OCH_2 + 2CH_3NH_2 \rightarrow (NH_2)(CN)COC(NH_2)(CN) + 4CH_4 + 2CH_3CN \quad -30\ \text{kcal/mol} \quad (8)$$

$$CH_2OCH_2 + CH_3Ph \rightarrow PhCHOCH_2 + CH_4 \quad -16\ \text{kcal/mol} \quad (9)$$

A single cyano group is far more effective than a single

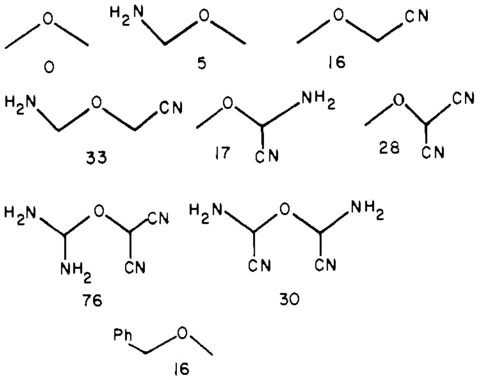


Figure 7. Stabilization energies (kcal/mol) of substituted carbonyl ylides relative to the parent.

amino group at stabilizing the carbonyl ylide (cf. (1) and (2)). A second cyano placed on the same carbon as the first (4) has a slightly larger stabilizing effect than when placed on the remote carbon (3), but the second cyano group has a smaller effect than the first in either case. The "push-pull" stabilization is manifested by the effect of attaching a cyano group to the aminocarbonyl ylide (**5** and **6**). Attachment of cyano at C-3 affords an additional 28 kcal/mol, but at C-1 only 12 kcal/mol. The former stabilization is much larger than the influence of cyano on the parent, while the latter is smaller. The same conclusion can be made from a comparison of the effect of substitution of amino on the parent or on cyanocarbonyl ylide. The effect of placing two aminos and cyanos on opposite ends of the ylide is an enormous stabilization. If one assumes that a cyano provides three times the stabilization of one amino (from eq 1 and 2), then each amino provides 9.5 kcal/mol of stabilization and each cyano provides 28.5 kcal/mol of stabilization. On the other hand, symmetrical tetrasubstitution results in only 3.8 kcal/mol per amino and 11.3 kcal/mol per cyano group, or 2.5 times less stabilization.

These trends can be rationalized readily through a simple perturbation model. Figure 8 shows the STO-3G molecular orbitals of the parent carbonyl ylide and the relevant substituent orbitals, as well as those of various substituted ylides. Carbonyl ylide is a very electron-rich species, having a high-lying HOMO and low-lying LUMO.[17] The LUMO—a relatively low lying π^* orbital—of the cyano group has the major effect on the carbonyl ylide π MOs. Both the HOMO and LUMO energies of the carbonyl ylide are lowered, the LUMO more than the HOMO, by the cyano group. The acceptor orbital of the cyano group causes the LUMO of the ylide to be mixed into the HOMO in a positive fashion at the site of substitution, and the HOMO to be mixed into the LUMO in a negative fashion.[34] Thus, the frontier orbital polarization shown in Figure 8 for cyanocarbonyl ylide can be rationalized readily. The stabilization of the ylide upon substitution of the cyano group arises from the stabilization of the ylide HOMO by mixing with the cyano LUMO.

The amino group has exactly the opposite effect on the ylide frontier MO energies and coefficients. Because the nitrogen lone pair of the planar amino group is the only orbital of π symmetry to mix with the ylide HOMO and LUMO, both of these ylide frontier MOs are pushed up in energy, the HOMO more than the LUMO. The polarization of the aminocarbonyl ylide MOs is due to the fact that the donor group causes the ylide LUMO to mix into the ylide HOMO in a negative fashion at the site of substitution, and ylide HOMO to mix into the LUMO in a positive fashion.

It is interesting to note that the stabilized systems have smaller HOMO-LUMO gaps than the unstabilized parent. This seems to suggest that the thermodynamically stabilized systems will be more reactive toward both nucleophilic and electrophilic reagents than the less stable parent system. However, as noted in the previous section, the parent system is best considered a linear combination of two configurations. In the doubly excited configuration, the HOMO is higher in energy, and the LUMO is lower, than these orbitals are in the ground configuration. In effect, the effective HOMO energy of the carbonyl ylide is higher than is indicated by the single configuration calculation, and the effective LUMO energy is lower. By contrast, CI is much less important in the substituted cases, as described later. The effect of comparing the single configuration calculations for parent and substituted derivatives is to overestimate the HOMO-LUMO gap in the parent.

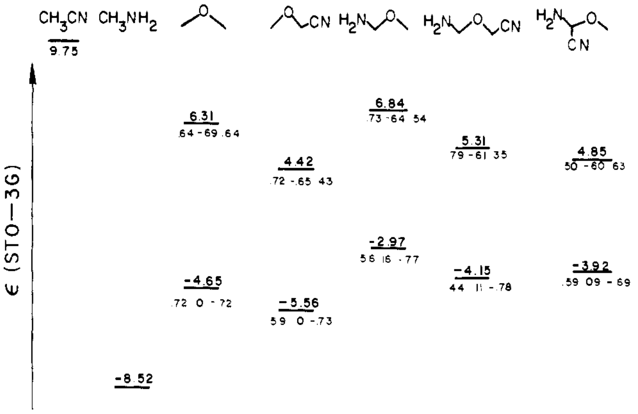


Figure 8. Frontier molecular orbitals of several carbonyl ylides and substituents.

Turning to the simultaneous substitution of both a donor and an acceptor group on the carbonyl ylide, it is clear from both orbital energies and polarizations that substitution of a donor on the unsubstituted carbon of cyanocarbonyl ylide, or of an acceptor on the unsubstituted carbon of aminocarbonyl ylide, will have a greater stabilizing effect than substitution of either group on the parent. This arises because of two effects: (1) the interaction of the amino group HOMO with the cyanocarbonyl ylide LUMO is increased due both to the small donor-HOMO, ylide-LUMO gap and to the large coefficient at the unsubstituted carbon of the ylide LUMO, and (2) at the same time, there will be less closed-shell repulsion arising from overlap of the donor HOMO with the ylide HOMO because of the smaller coefficient at the unsubstituted carbon of the HOMO. Substitution of an acceptor on the unsubstituted carbon of aminocarbonyl ylide leads to large stabilization due to the small acceptor-LUMO, ylide-HOMO gap and to the large HOMO coefficient at the unsubstituted carbon of the aminocarbonyl ylide.

Such a treatment immediately explains why substitution of both donor and acceptor at the same carbon is less effective in providing stabilization than is substitution at opposite ends of the molecule. Although the donor-HOMO, ylide-LUMO and acceptor-LUMO, ylide-HOMO gaps are identical no matter where the substituent is to be placed, maximum stabilization arises only when the substitutent is placed so as to overlap effectively with the appropriate ylide frontier orbital. That is, a donor provides maximum stabilization when placed at the site of largest LUMO coefficient, and the acceptor provides largest stabilization when placed at the site of largest HOMO coefficient.

Attachment of two cyanos at the same carbon (eq 4) leads to somewhat higher stabilization than does 1,3-dicyano substitution (eq 3). This can be directly related to the fact that a cyano group causes the larger HOMO coefficient to be located at the carbon to which it is attached. A second cyano attached here provides more stabilization due to greater overlap with

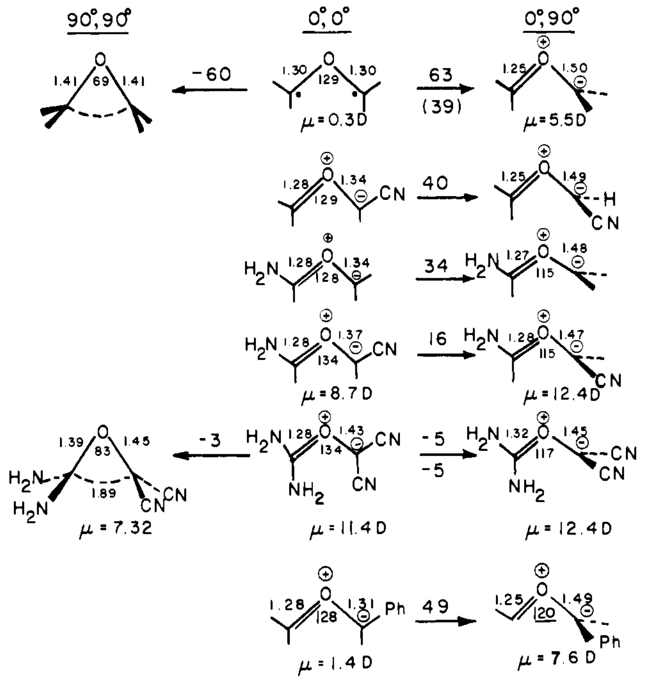


Figure 9. Geometries and barriers to rotation of carbonyl ylides. Energies above arrows are STO-3G; those below arrows are 4-31G.

the HOMO. A second cyano at the remote carbon provides less overlap with the HOMO and less stabilization.

Since the majority of carbonyl ylides studied experimentally have one or more phenyl substituents, model calculations were carried out on phenylcarbonyl ylide. Although phenyl may act as a donor or an acceptor, attachment of phenyl to an electron-rich system should cause the acceptor character of the phenyl to be emphasized. In other words, the high-lying carbonyl ylide HOMO will interact with one of the phenyl LUMOs more than the carbonyl ylide LUMO will interact with one the phenyl HOMOs, although both of these interactions will occur to some extent. In fact, the ylide stabilization caused by phenyl substitution is accidentally identical with the stabilization caused by cyano, and much larger than stabilization caused by amino.

Geometries and Isomerization Energies of Substituted Carbonyl Ylides. Figure 9 shows the partially optimized geometries of 0°,0° and 0°,90° forms of a selection of carbonyl ylides, as well as energies of rotation by STO-3G and, for the parent and tetrasubstituted compound, by 4-31G. Considering first the geometries of the planar species, substitution of a cyano group for hydrogen causes a lengthening of the adjacent CO bond and shortening of the remote CO bond, while the amino group has exactly the opposite effect. Phenyl resembles cyano in its influence on distortions, just as it resembles cyano in its ability to stabilize the ylide. The origin of these distortions is related to the change in coefficients described in connection with Figure 8. A donor (amino) group at the "left-hand" carbon, or acceptor (cyano or phenyl, in this context) at the "right-hand" carbon causes mixing of the LUMO into the HOMO with same coefficient signs at the "right-hand" carbon. As shown in Figure 10, this not only increases the HOMO coefficients at atoms 2 and 3 and decreases that at atom 1, but increases bonding between atoms 1 and 2 and increases antibonding (equivalent to decreases bonding) between atoms 2 and 3. The resulting geometries are distorted in the direction dictated by changes in bond strength; that is, the "right-hand" weakened bond is stretched and the "left-hand" strengthened bond is contracted. This is, of course, equivalent to noting that resonance structure $DCH{=}O^{+}{-}{}^{-}CHA$ (but not $DC^{+}H{-}O{-}{}^{-}CHA$) is an increasingly important contributor relative to $DC^{-}H{-}O^{+}{=}CHA$. The π charge distributions in the various species also support the interpretation that $DCH{=}O^{+}{-}{}^{-}CHA$ is a reasonable, if oversimplified, representation of the planar conformations of the unsymmetrical species.

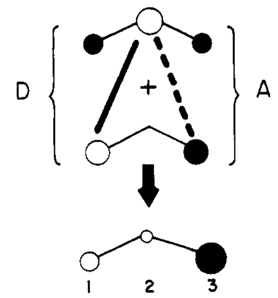


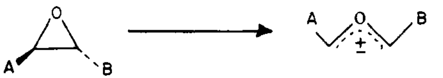
Figure 10. Mixing of LUMO into HOMO causes increase of 1-2 bonding and 2-3 antibonding.

The 1-amino-3-cyanocarbonyl ylide and the tetrasubstituted analogue become, through these geometrical distortions, closer in character to the traditional zwitterionic representation of carbonyl ylides. The charge separation is more appreciable, even in the planar form, as reflected in the dipole moments shown in Figure 9. The charges on atoms 1 and 3 in the planar 1-amino-3-cyano ylide are +0.25 and −0.09, respectively, and are +0.36 and −0.21 in the perpendicular conformation, as compared to −0.32 at both carbons for the parent. These charges do not fully reflect the charge separation, since most of the negative charge on the cyanomethylene terminus is dispersed onto the cyano carbon and nitrogen. The amino-substituted carbon bears considerable positive charge, since less charge is dispersed onto the amino nitrogen.

Upon rotation to the 0°,90° geometry, the shorter bond does not change appreciably, but the longer bond stretches considerably. Although there were convergence problems in calculations on some of the perpendicular species, it was possible to calculate the barrier to rotation of the NH_2CH terminus of 1-aminocarbonyl ylide. This barrier, 57 kcal/mol, is appreciably higher than that of CH_2 rotation in the same ylide (34 kcal/mol), and is not much less than that in the parent species. The amino group lowers the barrier to rotation of the adjacent bond, apparently because, although a partial CO double bond must be disrupted, the ability of amino to stabilize the positive charge which builds up on C-1 upon rotation apparently more than offsets this.

Rotation becomes successively easy as donor or acceptor substituents are added, until, in the 1,1-diamino-3,3-dicyanocarbonyl ylide, the 0°,90° species is more stable than the planar species. The decrease in barrier to rotation upon substitution of donors at 1 and acceptors at 3 has the same origin as the bond-length changes described above. In the tetrasubstituted extreme, the 2-3 antibonding causes the perpendicular conformation to become more stable than the planar. In simpler terms, 1-2 has become a double bond, and 2-3 has become a single bond which adopts the sterically least hindered conformation. This species resembles the highly substituted thiocarbonyl ylide described by Arduengo and Burgess.[22]

Rotation of the tetrasubstituted compound to the 90°,90° conformation and optimization of CO lengths and the COC angle give a species resembling a stretched oxirane. This should collapse without activation to the corresponding oxirane, if the termini were allowed to relax from planarity. By comparison to similar calculations on the unsubstituted compound, it can be seen that the oxirane with such extreme donor-acceptor character should open very easily to the corresponding nonplanar carbonyl ylide. These calculated quantities can be indirectly compared to Huisgen's measurements on 1-cyano-



A	B	STO-3G	4-31G
H	H	90	63
NH$_2$	H	89	62
H	CN	76	50
NH$_2$	CN	64	
Ph	H	76	
CN	CN	67	

Figure 11. Calculated energies of conversion of oxiranes to carbonyl ylides.

1,3-diphenylcarbonyl ylide, which has free energies of activation for rotational isomerization of 8–13 kcal/mol.[7]

Formation of Carbonyl Ylides from Oxiranes

The conversions of oxiranes to carbonyl ylides are electrocyclizations, and, since these reactions formally involve four electrons, they are thermally allowed for conrotatory motion and photochemically allowed for disrotatory motion. Huisgen[7] and others[35] have discussed the Woodward–Hoffmann correlation diagrams for these reactions, Devaquet et al. have verified that the parent compound should open thermally in a conrotatory fashion and photochemically in a disrotatory fashion,[8] and experimental verifications of the predicted modes of electrocyclization have been obtained for substituted oxiranes under thermal[7,36,37] and photochemical[7,38–40] conditions. Evidence has also been obtained for photochemical ring opening of the oxirane not only upon direct irradiation but also upon triplet sensitization.[39,41] Lee found that acetone-sensitized irradiation of *cis*- or *trans*-stilbene oxide produced the same stereoisomeric mixture of adducts upon trapping with alkenes.

Our studies have focused on the influence that substituents have on the ease of CC cleavage. The parent oxirane is known to undergo reaction by C–O cleavage,[8,9] but substituents apparently facilitate CC over CO cleavage.

The calculated energies of reaction, given in Figure 11,[42] give a qualitative indication of the ease of ring opening. A donor substituent (NH$_2$) has a minor effect, a result of even less stabilization of the oxirane (4 kcal/mol) than the ylide (5 kcal/mol), while cyano and phenyl have a large effect on ring opening, since the stabilization of oxirane by these substituents (2 kcal/mol) is far less than the stabilization of carbonyl ylide (16 kcal/mol). The 4-31G calculations were not performed on the larger molecules, but the changes in energies of reaction are nearly identical where comparisons are available. Assuming that 4-31G calculations are more nearly correct, the energy of opening of the 1-amino-3-cyano ylide should be 32 kcal/mol.

Two systems have been studied experimentally. *trans*-α-Cyanostilbene oxide (2-cyano-2,3-diphenyloxirane) has an activation enthalpy for conrotatory ring opening of 30.1 kcal/mol, and the free energy of the ylide has been estimated to be 18–22 kcal/mol above the oxirane. The *trans*- and *cis*-2-phenyl-3-*p*-tolyloxiranes racemize with activation energies of 37.4 and 42.6 kcal/mol, respectively.[43] The additional cyano group present in Huisgen's 2-cyano-2,3-diphenyloxirane lowers the experimental activation energy of opening by 7–13 kcal/mol. Our calculations indicate that one cyano group lowers the energy of oxirane ring opening by 14 kcal/mol, but attachment of cyano to a substituted oxirane should cause it to have a smaller effect.

The influence of multiple donor or acceptor substitution was qualitatively assessed by calculations on the ring opening of *trans*-2,3-dicyanooxirane to form *exo,exo*-1,3-dicyanocarbonyl ylide. Whereas the energy for ring opening of the monocyanooxirane is 76 kcal/mol by STO-3G, that for the dicyanooxirane is 67 kcal/mol at the STO-3G level. Whereas the first cyano group lowers the energy of ring opening by 14 kcal/mol, the second cyano group lowers the energy by only 9 kcal/mol. Thus, the energy of ring opening of the cyanodiphenyloxirane should be approximately 27 − 9 = 18 kcal/mol.

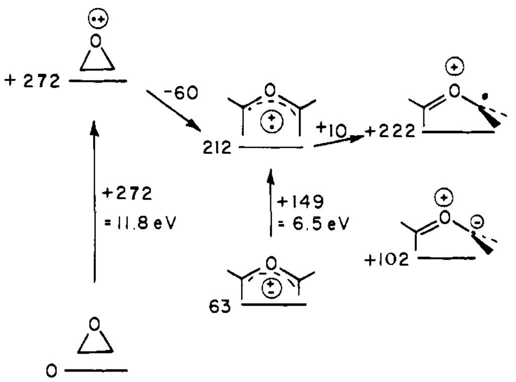


Figure 12. Relative energies (4-31G, kcal/mol) of species involved in electron transfer photosensitized reactions.

Albini and Arnold recently observed the generation of carbonyl ylides by photosensitized electron transfer irradiation.[44a] They found that irradiation of *cis*- or *trans*-diphenyloxirane in the presence of electron-accepting aromatics such as 1,4-dicyanobenzene produced carbonyl ylides, which could be trapped by electron-deficient alkenes. The mechanism of this reaction involves electron transfer from the oxirane ground state to the excited aromatic. The oxirane radical cation then opens to the carbonyl ylide radical cation, which then recaptures an electron and undergoes normal ylide reactions.

We have carried out calculations on the radical cations of the parent species. Figure 12 summarizes 4-31G calculations on each of these species. The calculated ionization potential of oxirane is relatively close to that (11.9 eV) measured experimentally.[45] The ring opening is exothermic because of the very low ionization potential of carbonyl ylide. We also find that the barrier to rotation in the radical cation of carbonyl ylide is very low, perhaps accounting for the lack of stereospecificity in reactions of the cis and trans diphenyloxiranes.[44]

Recently, complete 4-31G geometry optimizations by Bouma, MacLeod, and Radom have been reported which indicate that the carbonyl ylide radical cation is actually a nonplanar species having one terminus rotated 90° and pyramidalized.[44b] This species is 15 kcal/mol lower in energy than the optimized oxirane radical cation. Experimental ICR data suggest a difference of 26–29 kcal/mol.[44b,c] The nonplanar nature of the carbonyl ylide radical cation nicely accounts for the lack of stereospecificity in cycloadditions involving this radical cation as a carbonyl ylide precursor.[44a]

Cycloadditions of Carbonyl Ylides

Since most carbonyl ylides, except those extraordinarily push–pull substituted, will be planar, they are expected to undergo typical stereospecific concerted 1,3-dipolar cycloadditions.[5,17] Since even moderately push–pull substituted species are calculated to have substantial dipole moments (μ(H$_2$NCHOCHCN by STO-3G) = 8.7 D), polar solvents may well slow the cycloadditions of these species.

In order to better assess the electrophilicity (electron deficiency) or nucleophilicity (electron richness) of carbonyl ylides relative to alkenes, the HOMO and LUMO energies of carbonyl ylide and three substituted derivatives are shown in Figure 13. The STO-3G orbital energies have been corrected in the following way: in earlier calculations on a variety of 1,3 dipoles, reasonable estimates of experimental ionization potentials and electron affinities of these species, including car-

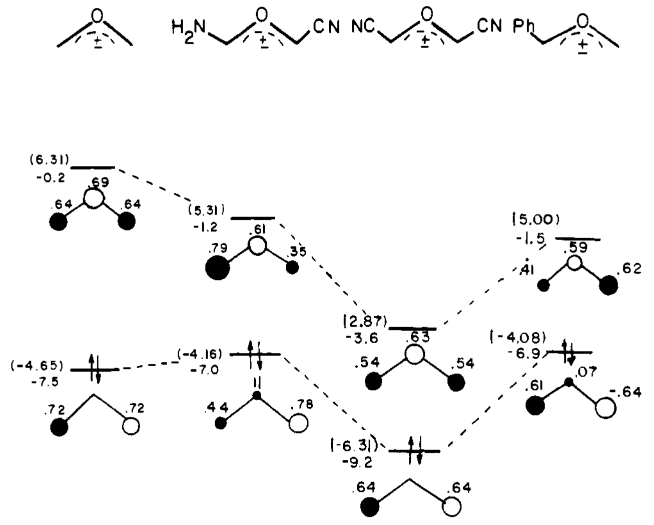


Figure 13. Frontier molecular orbitals of representative carbonyl ylides. The upper numbers (in parentheses) and coefficients are calculated by STO-3G, while the lower numbers are based on the estimated IP and EA of the parent.[17]

bonyl ylide, were obtained.[17] In Figure 13, the negatives of the estimated IP and EA of the parent carbonyl ylide are given for the HOMO and LUMO energy, respectively, and the changes in orbital energies upon substitution calculated by STO-3G are assumed to be correct. These estimated quantities are quite different from our earliest estimates.[17b]

As can be seen in the diagram, the parent carbonyl ylide is a very electron-rich species which is expected to react with electron-deficient alkenes such as acrylonitrile (IP = 10.9 eV, EA $\simeq$ −0.2 eV) or methyl acrylate (IP $\simeq$ 10.7 eV, EA $\simeq$ 0 eV) much more rapidly than with ethylene (IP = 10.5 eV, EA = −1.5 eV) or electron-rich alkenes such as methyl vinyl ether (IP = 9.1 eV, EA $\simeq$ −2 eV).[46] The push-pull substituted 1-amino-3-cyanocarbonyl ylide, and phenylcarbonyl ylide, both have higher lying HOMOs and lower lying LUMOs than the parent species and might be expected to react with both electron-rich and electron-deficient species. In both of these molecules, the ylide HOMO has been raised by donor orbitals (NH_2 or Ph) while the LUMO has simultaneously been lowered by acceptor LUMOs (CN or Ph). Since the parent is electron rich, these species are also expected to be predominantly electron rich, but relatively more reactive toward electron-rich species, as well. Experimentally, the ylide from stilbene oxide prefers addition to electron-deficient species,[33,41] as do ylides from simple alkyl or aryl oxiranes.[47]

Addition of two cyano groups lowers both the LUMO and HOMO considerably to give a species much more electrophilic than the parent. Hamberger and Huisgen have found that the somewhat analogous 1,3-dicyano-1,3-diphenylcarbonyl ylide, which should have a smaller gap and be both electrophilic and nucleophilic, reacts with both electron-rich and electron-deficient alkenes.[48]

Tetracyanocarbonyl ylide is an electron-deficient species, reacting considerably more rapidly with electron-rich alkenes than with electron-deficient alkenes.[2,49] The calculations on 1,3-dicyanocarbonyl ylide already indicate a dramatic HOMO and LUMO lowering, and two more cyanos are expected to obliterate any nucleophilicity and exacerbate the electrophilicity of this species. Since the EA of ethylene is at −1.5 eV and is increased to +2.9 eV by four cyano groups,[50] one might anticipate that the EA of carbonyl ylide (~0.2 eV) would be raised to 4.6 eV by four cyano groups. That is, this species should have a LUMO energy of about −4.6 eV. Unfortunately, convergence problems prevented successful calculations on this species.

The regioselectivity of cycloadditions of unsymmetrical ylides can be readily rationalized in terms of the HOMO and LUMO coefficient polarization described earlier. Like other 1,3 dipoles, the most nucleophilic terminus—that is, that with the larger HOMO coefficient—is the more electronegatively substituted terminus.[17] Thus, electrophiles, or the more electrophilic terminus of an electron-deficient alkene or unsaturated species, will become attached to the carbon bearing acceptor groups. On the other hand, the more electropositive terminus has the larger LUMO coefficient and will be the site of attack by nucleophiles or the more nucleophilic terminus of electron-rich alkenes. This generalization seems to satisfactorily account for experimentally observed regioselectivity.[5,41]

Many of the carbonyl ylides studied experimentally are aryl substituted. The effect of a conjugating group such as phenyl is to raise the HOMO and lower the LUMO of a π system to which it is attached. This is accompanied by stabilization arising from aryl HOMO-ylide LUMO and aryl LUMO-ylide HOMO interaction, and polarization of both the HOMO and LUMO so that the larger terminal coefficient is on the remote terminus in both. Such species are expected to react with both nucleophilic and electrophilic reagents at the unsubstituted terminus.

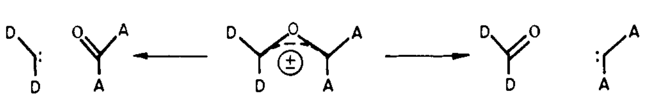
Fragmentation of Carbonyl Ylides

Experimental data suggest that the fragmentation of carbonyl ylides to carbonyl and carbene moieties is an excited-state process: whereas photochemical generation of carbonyl ylides is accompanied by fragmentation,[6] the thermal generation of carbonyl ylides in the presence of alkenes gives cycloadditions cleanly, unaccompanied by fragmentation.[7] There are two obvious possible explanations for why the fragmentation might occur photochemically, but not thermally: (1) the fragmentation is highly endothermic, or (2) the fragmentation has a high activation energy because it is thermally forbidden in the Woodward-Hoffmann sense. A second phenomenon of interest is the propensity of carbonyl ylides to fragment between oxygen and the more electronegatively substituted terminus.[6] Again, this might have a thermochemical origin, although our studies suggest that this is more intimately connected to the nature of the excited state involved in the fragmentations.

For the parent oxirane, Devaquet et al. found that the one-step fragmentation to formaldehyde plus $^1A_1$ methylene is not only highly endothermic (by 118 kcal/mol), but is symmetry forbidden and has an activation energy of 140 kcal/mol.[9] Devaquet's estimates are somewhat too high, since full optimization was not carried out: using 101 kcal/mol for the heat of formation of $^3B_1$ CH_2,[51] 9 kcal/mol for the singlet-triplet gap, −26.0 kcal/mol for the heat of formation of formaldehyde,[26] and −12.6 kcal/mol for the heat of formation of oxirane,[27] this reaction is estimated to be endothermic by 88 kcal/mol. Devaquet found various one-step excited pathways for fragmentation but all appear to involve highly excited states, or inefficient pathways.[9]

Two-step pathways from oxirane, through the carbonyl ylide, are also thermally unfavorable for the parent species, involving an overall calculated activation energy of 142 kcal/mol.[9] However, excited states of oxirane may give a chemically activated carbonyl ylide with enough internal energy to traverse the barrier (41 kcal/mol) calculated for the second step.[9] Unfortunately, these authors did not consider the pathway which experimental evidence indicates is most likely to occur in substituted cases: photoexcitation of a planar (0°, 0°) carbonyl ylide, followed by fragmentation of the exicted state.

The calculated energies of fragmentation for the various



38	H, H	H, H	38
50	H, H	H, CN	41
64	H, H	CN, CN	41
42	CN, H	H, CN	42
-17	NH_2,H	H, H	20
7	NH_2,H	H, CN	32
14	NH_2,NH_2(⊥)	CN, CN	50
37	Ph, H	H, H	45

Figure 14. Energies of fragmentation (STO-3G) of carbonyl ylides to carbonyl and carbene fragments.

carbonyl ylides are given in Figure 14. These calculations were all performed at the single-determinant STO-3G level, using standard geometries for substituents, but otherwise optimized carbonyl ylides and singlet methylenes, and standard geometries for the carbonyl fragments. Owing to the lack of full geometry optimizations, and the crudeness of minimal basis calculations for bond-breaking processes, the absolute energies of reaction are not expected to be particularly reliable, but the trends upon substitution should be reasonable.

Based on the heats of formation of formaldehyde and methylene given above, and our previous estimate of the heat of formation of planar carbonyl ylide, this fragmentation is endothermic by 37 kcal/mol. This is remarkably close to the STO-3G calculated value (+38 kcal/mol). Even if the reaction were thermally allowed, this is too high an energy for the fragmentation of simple ylides to be observed thermally under conditions generally used for formation of the ylides.

Attachment of a single cyano group causes fragmentation in the direction of formation of cyanocarbene to be unchanged relative to the parent, but fragmentation to the left is disfavored. This arises because CN stabilizes carbonyl ylide and methylene to the same extent, but stabilizes formaldehyde much less. A second cyano group more than doubles this effect. Attachment of amino has a huge effect on fragmentation energies in both directions, because the carbonyl ylide is influenced very little by the amino group, but the aminocarbene is stabilized to a very large extent, and formaldehyde to a moderately large extent. The 1-amino-3-cyano compound is more difficult to cleave, since the push-pull stabilization of the ylide decreases the ease of both fragmentations. The fully substituted compound has a large preference for cleavage to the left, primarily due to the very large stabilization of the carbene by the amino groups.

The phenyl carbonyl ylide prefers to fragment in such a way as to form phenylcarbene. The analogy to the cyano group breaks down at this stage, presumably because phenyl can substantially stabilize the carbene.

These calculations suggest that the thermochemically preferred mode of fragmentation is between oxygen and the more electropositively substituted terminus, that is, opposite to the direction observed experimentally by Griffin and co-workers under photolytic conditions.[6] Only in the phenyl-substituted case is the direction of cleavage similar to that observed experimentally. In general, the difference between the thermochemical predictions and experiment supports the notion that the fragmentation is an excited-state, rather than a ground-state, process, since product stabilities do not determine the preferred mode of cleavage.

Correlation diagrams for this process confirm that the fragmentation is thermally forbidden. Figure 15 shows the orbital correlation diagram for fragmentation of the parent carbonyl ylide, retaining planarity throughout the reaction. Orbital energies are from STO-3G calculations. The ground configuration of the ylide correlates with the ground state of formaldehyde and the $n_s^0n_p^2$ doubly excited singlet of methylene. That is, the thermal reaction to form the lowest singlet states of both fragments is forbidden. At the state correlation diagram level, the formation of the doubly excited singlet carbene would be avoided, since the $n_s^2n_p^0$ and $n_s^0n_p^2$ configurations cross and are of the same symmetry.

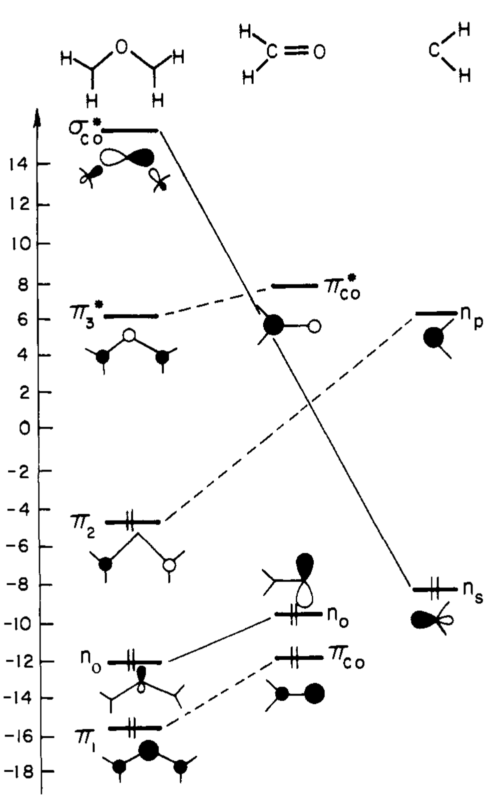


Figure 15. Orbital correlations diagram for planar fragmentation of carbonyl ylides. Full lines show correlations between σ orbitals; dotted lines show correlations between π orbitals.

Although small deviations from planarity destroy the orbital crossings in a formal sense, the energetics of the reaction will not be significantly changed, since surface crossings will be replaced by surface "touchings", and substantial barriers to reaction should still remain. Even though the parent carbonyl ylide has substantial diradical character, having some of the $\pi_2^0\pi_3^{*2}$ configuration mixed into the ground configuration, the $\pi_2^0\pi_3^{*2}$ configuration correlates with an even more highly excited state of the products.

The forbiddenness of this fragmentation is closely related to the forbidden least motion addition of carbenes to alkenes.[52] In order for the fragmentation to occur, appreciable out-of-plane distortion of the methylene fragment must occur as the CO bond breaks.

Most theoretical discussions of photochemical reactions indicate that photochemical reactions occur by crossing of a reactant excited state surface with a doubly excited state surface that correlates, in turn, with the product ground state.[53] Confining our attention to the lowest singlet states of products, we note that the lowest singlet state of products correlate with a double excited state, $\pi_2^0\sigma_{CO}^{*2}$, of reactants.

The calculations of Devaquet et al. indicate that both the first and second lowest excited singlet states are $\pi\pi^*$ states.[8] These, like the ground and the aforementioned doubly excited states, are all symmetric with respect to the plane of carbonyl ylide, and will mix upon CO stretching. The $\pi^0\sigma_{CO}^{*2}$ state will drop in energy drastically upon CO stretching. For example, an STO-3G calculation indicates that a σ^*_{CO} orbital becomes the LUMO of carbonyl ylide when one CO bond is stretched from its equilibrium value to 2.3 Å. (With this constraint, the other CO contracts to 1.24 Å and the COC angle to 119°.)

Based on Devaquet's calculations and Figure 15, the following scenario can be constructed for the photochemical cleavage of carbonyl ylides. The $\pi_2{}^1\pi_3{}^{*1}$ excited state mixes with the rapidly descending $\pi_2{}^0\sigma^*{}_{CO}{}^2$ state which correlates with the lowest singlet states of products. On the other hand, triplet $\pi\pi^*$ states, which Devaquet indicates are of very low energy,[8] should rotate to a perpendicular geometry as do alkene triplets and then intersystem cross to the planar ground state singlet.

Finally, we comment briefly on the influence of substituents on the ease and direction of fragmentation of carbonyl ylides. Most substituents influence the HOMO and LUMO of carbonyl ylide in such a way so as to narrow the HOMO–LUMO gap, which should lower the $\pi_2 \rightarrow \pi_3{}^*$ transition energy. Furthermore, many of the substituted ylides which have been studied are expected to form ground state singlet carbenes upon fragmentation, and for such species the $\pi\pi^*$ singlet state of the carbonyl ylide is expected to lead to facile fragmentation, as usual via evolution into a $\pi_2{}^0\sigma_{CO}{}^{*2}$ state.

As noted earlier, the direction of unsymmetrical carbonyl ylide fragmentation can be simply generalized: fragmentation occurs at the most electronegatively substituted terminus.[54] For an unsymmetrical system such as cyanocarbonyl ylide or aminocarbonyl ylide, the O–C bond to the more electronegative terminus is longer than the other O–C bond, and the lowest $\sigma^*{}_{CO}$ orbital is concentrated on the longer O–C bond. The lowest $\pi_2{}^0\sigma_{CO}{}^{*2}$ state will be lowered in energy by stretching the O–C bond to the most electronegative terminus, so that cleavage of the excited state will occur at that terminus. The experimentally observed direction of fragmentation[6] can be satisfactorily explained in this way.

The fragmentation of diazomethane has been studied too frequently to be reviewed here,[55] but the conclusions about thermal barriers, and the necessity to bend the CH_2 group out of plane in the thermal reaction, and the excited states responsible for cleavage are similar to those described here for carbonyl ylides.

Conclusion

In this paper, a theoretical survey has been made of the dominant processes observed in carbonyl ylide chemistry. Owing to our heavy reliance on model systems, and use of rather approximate, even if ab initio, calculations, quantitative comparisons with experiment are not possible. Nevertheless, this work should provide a theoretically tenable framework with which to interpret the ever-widening experimental knowledge of the chemistry of one fascinating representation of the family of 1,3 dipoles, the carbonyl ylides.

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