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Orbital Symmetry Control in the Photochemistry of *trans*-2,3-Diphenyloxirane

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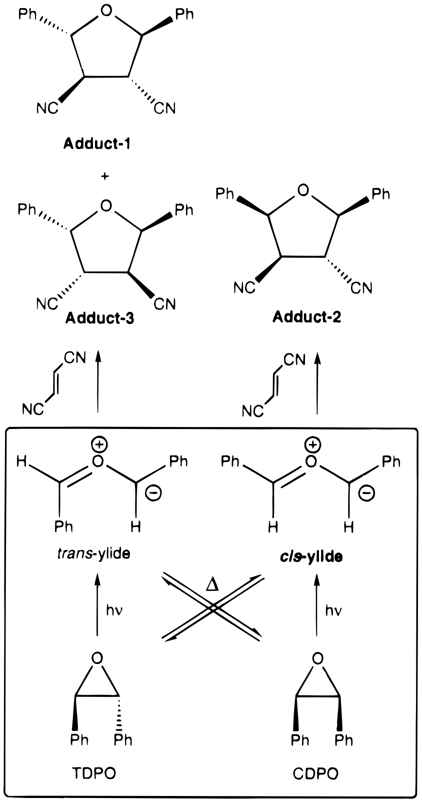
We report quantum yields following 266 nm photolysis of *trans*-2,3-diphenyloxirane (TDPO) for the formation of the *trans*-ylide (Scheme 1, $\Phi = 0.099 \pm 0.014$), *cis*-2,3-diphenyloxirane (CDPO, $\Phi = 0.10 \pm 0.009$), benzaldehyde ($\Phi = 0.47 \pm 0.04$), and deoxybenzoin ($\Phi = 0.077 \pm 0.002$). Photolysis of TDPO may lead to both orbital symmetry allowed and forbidden products, but the *trans*-ylide decays solely via an orbital symmetry predicted pathway to CDPO. Coupling our quantum yields to results of Das and co-workers,[1] we report an extinction coefficient for the *trans*-ylide of 9.4×10^4 M^{-1} cm^{-1} at 470 nm. We also report pseudo-first-order rate constants for the reaction between maleic anhydride and the *trans*-ylide in acetonitrile ($k_Q = 3.32 \pm 0.04 \times 10^9$ M^{-1} s^{-1}) and in cyclohexane ($k_Q = 5.36 \pm 0.07 \times 10^9$ M^{-1} s^{-1}) and between fumaronitrile and the *trans*-ylide in acetonitrile ($k_Q = 1.57 \pm 0.02 \times 10^9$ M^{-1} s^{-1}) and cyclohexane ($k_Q = 3.69 \pm 0.04 \times 10^9$ M^{-1} s^{-1}). We report the crystal structure of *rac*-(2*R*,3*R*,4*R*,5*R*)-3,4-dicyano-2,5-diphenyltetrahydrofuran, the sole product of 1,3-dipolarophilic addition between the *trans*-ylide and fumaronitrile in cyclohexane. A brief discussion of solvent and steric effects in 1,3-dipolarophilic additions is included.

1. Introduction

Both the thermal and photochemical ring openings of *trans*-2,3-diphenyloxirane (TDPO, Scheme 1), if concerted, are formal four-electron processes and, using the behavior of the cyclopropyl anion as a model, are predicted by orbital symmetry[2,3] to yield the *cis*-ylide (conrotatory) and *trans*-ylide (disrotatory), respectively (Scheme 1).[4−6] The *cis*-ylide and *trans*-ylide, from orbital symmetry arguments, should ring close thermally to the orbital symmetry allowed TDPO and *cis*-2,3-diphenyloxirane (CDPO), respectively.

The analogy between the cyclopropyl anion and TDPO is based on isoelectronics; however, among other differences, a lone pair centered on oxygen is significantly lower in energy than one centered on carbon and therefore the extent of coupling between the various orbitals involved in the ring-opening process may well be significantly different in the two systems. The concerted ring-opening process simultaneously stretches the C−C bond and rotates the methylene groups into conjugation with the oxygen lone pair. A nonconcerted pathway to ring-opening of TDPO would, perhaps, break the C−C bond either homo- or heterolytically, rotating (and depyramidalizing from sp^3 to sp^2 hybridization) one methylene group into conjugation with a filled n-orbital of the oxygen, leaving the second methylene group as either a radical or anion and yielding the *cis*- and *trans*-ylide with perhaps steric (but certainly not orbital symmetry) control of the stereochemistry. Such a pathway, especially if photochemical, is analogous to the photoheterolysis/homolysis observed for diphenylmethyl halides.[7,8] Note that whereas photoexcitation in the model cyclopropyl anion is a nominal $\sigma^* \leftarrow n$ transition localized in the three membered ring, photo-excitation of TDPO is a $\pi^* \leftarrow \pi$ transition initially localized in the phenyl rings. The symmetry of this excited state should be a sensitive

Scheme 1. Diagram of the Orbital Symmetry Controlled Reactions Studied in This Paper



[⊗] Abstract published in *Advance ACS Abstracts*, March 15, 1997.

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(4) We show only one isomer of the *cis*-ylide, the exo-exo isomer. A number of researchers[5,6] have noted that the endo-endo isomer would be less likely to form due to adverse steric interactions between the two phenyl rings.

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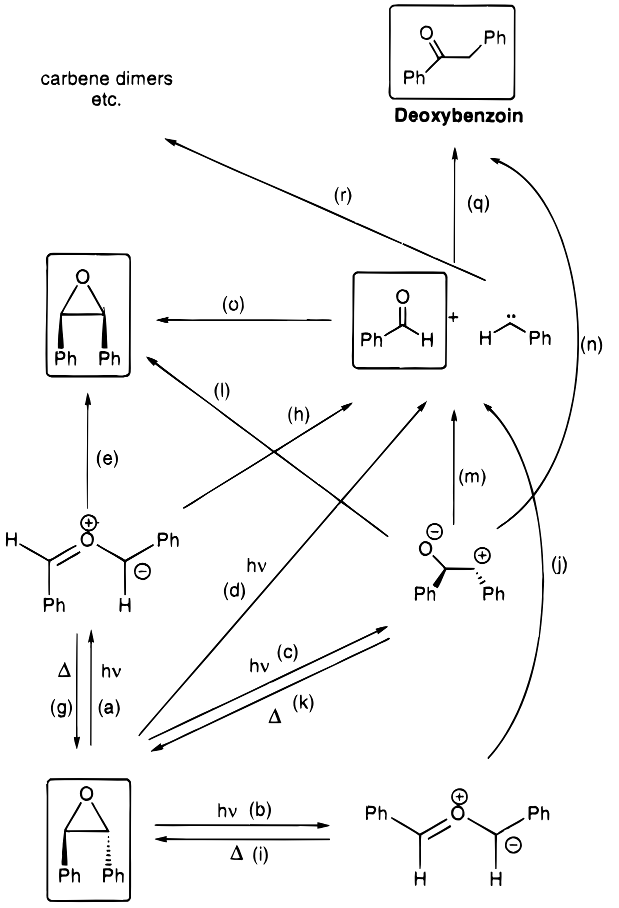
Scheme 2. Diagram of a Number of Mechanistic Pathways That May Be Invoked To Explain the Formation of the Products Oberved Following Photolysis of TDPO



function of the molecule's conformation, and transfer of excitation energy from the phenyl ring into the C−C antibonding orbital need not involve the oxygen lone pair. One goal of our study is to measure the concertedness of the photochemical ring-opening of TDPO.

The products that have been isolated upon photolysis of TDPO in both polar and apolar solvents are highlighted in Scheme 2. The specific pathways to these products will be reviewed later in this paper. Herein, we report quantum yields for the production of the *trans*-ylide, CDPO, benzaldehyde, and deoxybenzoin upon photolysis of TDPO in cyclohexane. In doing so, we clarify the thermal chemistry and photochemistry of *trans*-2,3-diphenyloxirane.

Finally, we initiated these studies with the hope of learning how solvent dynamics couple with an orbital symmetry controlled reaction path, specifically the ring-closure of the *trans*-ylide. Those studies, including a full Kramers analysis,[9,10] will be published separately.[11]

The *cis*- and *trans*-ylides were first observed optically following photolysis of the corresponding oxirane (Scheme 1) in glassy matrices at 77 K.[5,12−14] Both ylides display broad aborptions in the visible region, $\lambda_{\max}$ for the *cis*-ylide at *ca.* 500 nm and for the *trans*-ylide at *ca.* 470 nm. At room temperature, following photolysis of TDPO with 266 nm light in either acetonitrile or an alkane solvent, the characteristic absorption of the *trans*-ylide appears with a risetime of *ca.* 400 ps and decays with a half-life of *ca.* 500 ns.[1,15] Das and co-workers[1] note that the similar decay rates of this formally zwitterionic transient in both polar and nonpolar solvents is coincidental: a larger activation enthalpy in acetonitrile is offset by a larger (less negative) activation entropy.

A 266 nm photolysis of CDPO at room temperature produces the characteristic absorption of the *cis*-ylide in *ca.* 400 ps. This absorption decays with a half-life of *ca.* 50 ns, an order of magnitude more rapidly than that assigned to the *trans*-ylide. Our group and that of Das and co-workers tentatively invoked the lower steric congestion to the formation of the *trans*-oxirane to explain the large increase in reaction rate.

In picosecond pump-probe experiments, we[15] observed significant formation (*ca.* 15%, assuming equal extinction coefficients for the two ylides) of the formally forbidden *trans*-ylide upon photolysis of CDPO. We did not observe formation of the forbidden *cis*-ylide upon photolysis of TDPO perhaps because of a lack of time resolution in our experiment. Lee[16] used the dipolarophile methyl acrylate to trap the ylides formed upon photolysis of TDPO in acetonitrile and reports about 10% of the "forbidden" adducts.

In an elegant experiment, MacDonald and Crawford[17] thermolyzed chiral *trans*-2-tolyl-3-phenyloxirane at 200 °C to form the *cis*-ylide intermediate and report a relative rate of racemization of the starting oxirane to formation of the isomeric *cis*-oxirane of 172 to 1. This means that thermal ring-opening/ring-closing for the *trans*-diphenyloxirane likely also follows orbital symmetry predictions and the *cis*-ylide does not isomerize to the *trans*-ylide. However, their thermolysis of chiral *cis*-2-tolyl-3-phenyloxirane is less conclusive, and they make no note of side products produced in the thermolysis.

2. Experimental Section

2.1. Solvents, Reagents, and Products. All alkanes and cycloalkanes used in this study were purified by passage through silver nitrate-impregnated alumina.[18] Other methods of purification such as reflux over sulfuric acid followed by distillation from lithium aluminum hydride lead to irreproducible results. Cyclohexane and heptane were from Aldrich, HPLC grade. Hexane, tetradecane, and hexadecane were from Aldrich, 99%. Acetonitrile was Burdick and Jackson, UV-grade, and was used as received. TDPO and CDPO, from Aldrich, were recrystallized from hexanes. Maleic anhydride, benzaldehyde, and deoxybenzoin, all from Aldrich, were used as received. Fumaronitrile, Aldrich, was sublimed prior to use. Ferric sulfate, 1,10-phenanthroline, and EDTA were from Aldrich, highest purity available, and were used as received.

Adducts **1**, **2**, and **3** (Scheme 1) were synthesized as follows. An acetonitrile solution of TDPO (0.1 M) and fumaronitrile (0.1 M) was photolyzed (Rayonet Photoreactor, four lamps, 254 nm) to <10% conversion. The adducts were purified by silica column chromatography (methanol/ethyl acetate/hexanes as eluent) and identified by GC/MS (HP5988A, HPULTRA2 column) ($M^{+\bullet} = 274$) and proton NMR (400 MHz). Adduct **1**

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was further identified by X-ray crystallography.[19] The NMR assignments are as follows: Adduct **1** (*rac*-(2*R*,3*R*,4*R*,5*R*)-3,4-dicyano-2,5-diphenyltetrahydrofuran): ^{1}H (CDCl$_3$) δ 7.6−7.4 (m, 10H, aromatic), 5.6−5.4 (m, 2H, benzylic), 3.6−3.4 (m, 2H, methylenic). Adduct **2** (*rac*-(2*S*,3*R*,4*R*,5*R*)-3,4-dicyano-2,5-diphenyltetrahydrofuran): ^{1}H (CDCl$_3$) δ 7.6−7.4 (m, 10H, aromatic), 5.34 (d, $J = 6.7$ Hz, 1H, benzylic), 5.15 (d, $J = 7.8$ Hz, 1H, benzylic), 3.86 (dd, $J = 6.7$ Hz, 5.2 Hz, 1H, methylenic), 3.40 (dd, $J = 7.8$ Hz, 5.1 Hz, 1H, methylenic). Adduct **3** (*rac*-(2*R*,3*S*,4*S*,5*R*)-3,4-dicyano-2,5-diphenyltetrahydrofuran): ^{1}H (CDCl$_3$) δ 7.6−7.4 (m, 10H, aromatic), 5.81 (d, $J = 4.8$ Hz, 2H, benzylic), 3.93 (d, $J = 4.8$ Hz, 2H, methylenic). We have been unable to model the splitting between the benzylic and methylenic protons in Adduct **1**. The NMR spectra of all three adducts are included as supporting information.

2.2. Quantum Yields. All samples were agitated rapidly by magnetic stirrer in sealed 1 cm × 1 cm quartz cuvettes during photolysis. Oxirane solutions were bubbled with argon for 10 min prior to photolysis. Ferrioxalate solutions, used for actinometry, were prepared as per the literature.[20,21] Oxirane solutions were 0.01 M TDPO in cyclohexane or tetradecane, 0.005 M tetradecane or hexadecane as internal GC standard, 0 to 0.01 M maleic anhydride or fumaronitrile as quencher. At a 1 cm pathlength, 0.01 M TDPO solution is optically opaque at 266 nm. The 0.01 M maleic anhydride solutions in cyclohexane absorbs 266 nm light with an optical density of 0.04; fumaronitrile in cyclohexane is transparent at 266 nm.

We split the fourth harmonic of a Nd:YAG laser (Quanta-Ray DCR-I, 266 nm, 6 ns fwhm, 10 Hz) with a series of quartz flats such that a pair of samples receive roughly equivalent photon intensities (split ratio *ca.* 1.2:1). Laser power varied from 100 to 500 μJ/pulse from photolysis to photolysis and photolyses were carried to <3% conversion. In the regions sampled, we measured linear effects of both photon intensity and conversion on product quantum yields.

We measured the photoconversion of $Fe^{3+} \rightarrow Fe^{2+}$ by the absorption of the 1,10-phenanthroline complex of Fe^{2+} (HP8452A diode array spectrophotometer). Each optical density reported is the average of four measurements. Our uncertainty in the split ratio is given as one standard deviation from the average of nine photolyses of ferrioxalate solution and is ±6%.

Yields of photolysis products from oxirane solutions were measured by gas chromatography (HP5890, J&W Scientific DB5 or DB17 column, flame ionization detection (FID)). The peaks due to benzaldehyde, tetradecane, hexadecane, CDPO, TDPO, deoxybenzoin, and adducts **1**, **2**, and **3** were identified by injection of known samples and by GC-MS. FID response factors were measured relative to tetradecane. Phenylcyclohexylmethane, the product of phenylmethyl carbene insertion into cyclohexane was identified by GC-MS and by the observation that photolysis of TDPO in hexanes or heptane yielded different peaks, identifiable by their masses as carbene insertion into the respective solvents. We synthesized phenylcyclohexylmethane by condensation of cyclohexylmagnesium bromide (Aldrich) with benzyl chloride (Aldrich) in 20% yield. We were unable to purify the product to greater than 84% purity, however, and we therefore do not report quantum yields for this product.

Quantum yields reported are the average of three photolyses, two GC injections per photolysis. Reported errors are one standard deviation from the average of multiple photolyses.

2.3. Laser Flash Photolysis. Our laser flash photolysis experiment is similar to many reported in the literature[22] and will therefore only be described briefly. Samples are excited by the fourth harmonic of a Nd:YAG laser (typically 0.5 to 5 mJ/pulse) and probed by a pulsed high pressure mercury lamp.[22,23] Probe light wavelength is selected by a monochromator (Instruments S.A. Inc, Model H10) and detected as a function of time by a photomultiplier (Electron Tubes, Inc., model 9816, four dynodes wired). The output current of the photomultiplier is dropped over 50 Ω to ground, and the resulting voltage is measured with a digital oscilloscope (Tektronix, Model TDS350) and stored and processed on a PowerMac 7100.

Table 1. Pseudo-First Order Rate Constants Measured for the Reaction between Either Maleic Anhydride or Fumaronitrile and the *Trans*-Ylide in Either Acetonitrile or Cyclohexane

	acetonitrile	cyclohexane
maleic anhydride	$(3.32 \pm 0.04) \times 10^9$ M^{-1} s^{-1}	$(5.36 \pm 0.07) \times 10^9$ M^{-1} s^{-1}
fumaronitrile	$(1.57 \pm 0.02) \times 10^9$ M^{-1} s^{-1}	$(3.69 \pm 0.04) \times 10^9$ M^{-1} s^{-1}

Table 2. Quantum Yields for the Formation of the Products Listed Following Photolysis of TDPO in Cyclohexane in the Presence of Quencher (Q)

[Q] (M)	Φ_{CDPO}	$\Phi_{\mathrm{benzaldehyde}}$	$\Phi_{\mathrm{deoxybenzoin}}$	$\phi_{\mathrm{adduct}\ \mathbf{1}}$
0	0.10 ± 0.009	0.47 ± 0.04	0.077 ± 0.002	−
0.004[a]	0	0.44 ± 0.07	0.072 ± 0.006	−
0.002[a]	−[c]	0.47 ± 0.07	0.077 ± 0.006	−
0.0013[a]	−[c]	0.46 ± 0.07	0.076 ± 0.006	−
0.001[a]	−[c]	0.45 ± 0.07	0.074 ± 0.006	−
0.010[b]	0	0.47 ± 0.07	0.077 ± 0.006	0.099 ± 0.014

For these studies, all kinetic traces are modeled as first-order decays, and fits are minimized with the Levenberg−Marquardt algorithm.[24]

Samples were prepared so as to exhibit optical densities of 0.3 to 0.6 at 266 nm and were bubbled for 10 min prior to the experiment with solvent-saturated argon. In agreement with the literature,[1] atmospheric oxygen has no effect on the lifetimes or quenching rates we measure. We probe the *trans*-ylide produced upon photolysis of TDPO at 470 nm. Typically, the average of five laser pulses yielded acceptable signal to noise. Samples were not stirred during the experiment.

Concentrations of maleic anhydride or fumaronitrile as quencher were varied from 0 to 0.01 M in cyclohexane and acetonitrile. We report the pseudo-first-order rate of quenching (k_Q) of the *trans*-ylide by maleic anhydride in acetonitrile as $(3.32 \pm 0.04) \times 10^9$ M^{-1} s^{-1}, in acceptable agreement with the 3.0×10^9 M^{-1} s^{-1} previously reported by Das and co-workers.[1] Errors reported are one standard deviation in the linear fit to a Stern−Volmer lifetime analysis.

3. Results

3.1. Quenching Rate Constants. Table 1 lists the pseudo first order rates (k_Q) by which maleic anhydride and fumaronitrile quench the transient absorption assigned to the *trans*-ylide in acetonitrile and cyclohexane. The value we report for maleic anhydride in acetonitrile agrees with the 3.0×10^9 M^{-1} s^{-1} reported by Das and co-workers.[1]

3.2. Quantum Yields. Table 2 lists the quantum yields both in the absence and presence of quencher for photolysis of TDPO in cyclohexane. Because two products of the photolysis, benzaldehyde, and deoxybenzoin (Scheme 2) have slightly larger extinction coefficients at 266 nm than does TDPO ($\epsilon_{\mathrm{benz}} \approx \epsilon_{\mathrm{deox}} \approx 900$; $\epsilon_{\mathrm{TDPO}} = 740$),[14,20] we were unable to take the photoreaction to large enough conversion to confidently measure the quantum yield of disappearance of TDPO. Product quantum yields do not add to 1.

Upon addition of quencher, under conditions where CDPO is formed in concentrations too small to quantify,

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(19) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director of Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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we measure changes in the quantum yield of the other products that are smaller than experimental error. The highest concentration of maleic anhydride we were able to use in cyclohexane (0.004 M) is a nearly saturated solution at room temperature. We suggest that the small decrease in product quantum yields we measure under these conditions are not due to chemical quenching, but instead to the deposition of small amounts of the maleic anhydride onto the windows of our photolysis cell. In the presence of fumaronitrile, the quantum yield of adduct **1** equals the quantum yield of CDPO in the absence of quencher. In cyclohexane, we are unable to detect by GC the production of adducts **2** or **3** following photolysis of TDPO in the presence of fumaronitrile.

Although there is a literature report[16] of the isolation of the adduct of maleic anhydride and both the ***cis-*** and *trans*-ylide in acetonitrile, the method of isolation is not reported. By GC, we were unable to detect the production, in cyclohexane, of the adduct of maleic anhydride with either ylide presumably due to decomposition during workup.

In the relatively viscous alkane solvent tetradecane (hexadecane as internal GC standard), we measured the same quantum yield of benzaldehyde in the absence of maleic anhydride as in the presence of sufficient maleic anhydride to completely inhibit the production of CDPO.

Finally, while photolysis of TDPO in deoxygenated fumaronitrile-saturated (*ca.* 0.01M) cyclohexane yields only one of the three possible adducts, photolysis of TDPO in acetonitrile with 0.1 M fumaronitrile (air saturated) yields all three possible adducts in roughly equal yields.

4. Discussion

We set out to learn if the *trans*-ylide, once formed by photolysis of TDPO in alkane solvents, decays solely to form the orbital symmetry predicted product CDPO.[11] We have done so as follows. The electron deficient alkenes maleic anhydride and fumaronitrile undergo 1,3-dipolarophilic additon to the *trans*-ylide (Scheme 1) at near diffusion-controlled rates (Table 1). Concentrations of maleic anhydride in either cyclohexane or tetradecane high enough to quench every *trans*-ylide formed completely quenches the photoproduction of CDPO without affecting the yield of any of the other known products of TDPO photolysis.

This experimental finding precludes any thermal fragmentation or rearrangement of the *trans*-ylide (path h, Scheme 2). It does not, however, preclude the orbital symmetry forbidden closure of the *trans*-ylide to TDPO (path g) or its isomerization to the *cis*-ylide followed by closure to TDPO (paths f (not shown) and i). Concentrations of fumaronitrile in cyclohexane high enough to quench every *trans*-ylide formed quenches the photoproduction of CDPO and leads to the production of adduct **1** with a quantum yield experimentally equivalent to the quantum yield for production of CDPO in the absence of quencher. Since adduct **1** can seemingly only be formed by 1,3-dipolarophilic addition of fumaronitrile to the *trans*-ylide, we propose that the quantum yield of this adduct is the quantum yield of the *trans*-ylide. We therefore conclude that, within experimental error, every molecule of the *trans*-ylide formed in cyclohexane decays to CDPO.

The quantum yields we measure give us other information. Das and co-workers[1] measured the absorption of the *trans*-ylide at 470 nm as a function of the number of 266 nm photons used to excite TDPO in methylcyclohexane and report the product of the extinction coefficient times the quantum yield for production ($\epsilon_{\text{ylide}} \times \Phi$ylide) as 9.6×10^3 M^{-1} cm^{-1} (with an uncertainty of ±20%). With the assumption that the quantum yield for production of the *trans*-ylide is the same in methylcyclohexane and cyclohexane, we can calculate the extinction coefficient of the *trans*-ylide as 9.6×10^4 M^{-1} cm^{-1} at 470 nm in alkane solvents.

Our experiments also shed light on the other photoinitiated reactions of TDPO diagrammed in Scheme 2. Photolysis of TDPO produces CDPO, presumably via formation of the *trans*-ylide. Also produced in the photolysis are benzaldehyde, deoxybenzoin, and products due to the formation of phenylmethyl carbene. A number of pathways to these products have been proposed and are shown in Scheme 2. Photolysis of TDPO is known (a) to produce the *trans*-ylide which we have shown decays solely to CDPO. Photolysis may also lead to (b) formation of the *cis*-ylide, (c) heterolytic (or homolytic (not shown)) cleavage of a C−O bond, or (d) a concerted two-bond scission to form benzaldehyde and phenylmethyl carbene. The *cis*-ylide has a lifetime one-tenth that of the *trans*-ylide and perhaps also displays different chemistry than the *trans*-ylide. However, based on the work of MacDonald and Crawford,[17] if formed, the *cis*-ylide likely (i) decays to TDPO. The zwitterion formed via path c may ring close to (k) TDPO, (m) cleave to form benzaldehyde and phenylmethyl carbene, or (n) undergo a 1,2-hydride shift to form deoxybenzoin. The benzaldehyde/phenylmethyl carbene pair may recombine to form either (o) the *cis*-ylide or (q) deoxybenzoin, or (r) it may cage escape, in which case the carbene may undergo dimerization or insertion into solvent; we have shown that it does not recombine to form the *trans*-ylide.

Support for a number of these pathways exists in the literature. Of particular interest, Bigot and co-workers[25,26] have calculated the thermal and photochemical reaction pathways open to the parent oxirane, ethylene oxide. Among their conclusions, both thermally and photochemically, C−O bond rupture is favored over C−C bond rupture, although the species formed by the former path finds no barrier to reclosure. For thermal C−C bond rupture, conrotatory motion is favored over disrotatory motion, as predicted by orbital symmetry. For photochemical C−C bond rupture, the disrotatory process is favored, but only on the singlet manifold. The authors note that aryl substitution to the oxirane will stabilize the ylide formed upon C−C bond rupture and, for the photochemical process, may allow C−C rupture to compete with C−O rupture.

For the production of the carbonyl/carbene pair, Bigot and co-workers propose a possible two-bond scission via the excited single state of the oxirane. This conclusion is supported by the work of Clark and co-workers[27] who photolyzed *trans*-2,3-dinaphthyloxirane and observed the production of triplet naphthaldehyde. However, Das and co-workers[1] were unable to observe the formation of triplet benzaldehyde upon photolysis of TDPO.

Bigot and co-workers calculated that thermal pathways to the aldehyde/carbene pair following either C−C or C−O bond rupture appear to exhibit impassably high barriers.

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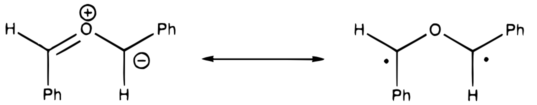
Scheme 3. Depiction of Two Resonance Structures That Contribute to the *Trans*-Ylide



Houk and co-workers[28] used *ab initio* calculations to study the effect of substitution on the chemistry of the ylides formed upon thermolysis of substituted oxiranes. They note that the unsubstituted ylide is best represented as 55% biradical/45% zwitterion (Scheme 3): phenyl substitution to the ylide significantly increases zwitterionic character, monosubstitution being more effective than 2,3-disubstitution. They further conclude that thermal fragmentation of the phenyl-substituted ylide is forbidden.

However, no calculations that we are aware of include interactions with solvent; and given even a nonpolar solvent's ability to stabilize charge separation[29] coupled to the at least partially zwitterionic nature of these ylides, gas phase calculations may not be perfect guides. Experimentally, Trozzolo and co-workers[5] estimate that photolysis of TDPO in ethanol glass at 77 K followed by warm-up yields 20−50 times more fragmentation products than photolysis alone, implying that fragmentation of the *trans*-ylide to benzaldehyde and phenylmethyl carbene may be a thermally activated process. And Warkentin and co-workers,[30,31] in a series of papers, have shown experimentally that in solution, alkoxy-substituted carbonyl ylides do thermally (and reversibly) fragment into a carbonyl/carbene pair.

The total product quantum yield of the photolysis of TDPO in cyclohexane is 0.65. Given the short (*ca.* 400 ps) lifetime of TDPO's excited state, we would not expect to observe significant fluorescence, and we are aware of no literature reports, including those of experiments run in glassy matrices at 77 K, for which fluorescence has been observed for the excited state of TDPO. While it is possible that the excited state intersystem crosses to the triplet manifold and then relaxes to the ground state with high efficiency, Lee[16] has shown that triplet sensitization of either TDPO or CDPO leads to product formation, though he does not report the quantum yield for these processes. We are not aware of any reports of the intersystem crossing rate of the excited state of an epoxide. Although excited states of aromatic ketones such as benzophenone intersystem cross in about 10 ps,[32] the excited singlet state of benzyl alcohol, which we feel is a better model for that of TDPO, displays a lifetime of 29 ns.[33] Therefore, assuming we and others in this field have not failed to isolate some other photoproduct, a significant percentage of photon energy is lost through internal conversion.

We suggest that orbital symmetry allowed closure of the *cis*-ylide to TDPO is the most plausible pathway for the observed internal conversion. Recombination of the benzaldehyde/phenylmethyl carbene pair or closure of the zwitterion formed via C−O bond rupture would presumably lead to formation of not just TDPO, but CDPO as well and we know experimentally that CDPO forms solely via the *trans*-ylide.

Although we have previously observed the formation of the *trans*-ylide upon photolysis of CDPO in cyclohexane,[15] we have no evidence for the production of the *cis*-ylide upon photolysis of TDPO. Photoproduction of the *cis*-ylide from TDPO need not contradict orbital symmetry predictions, it need only circumvent them. Photoexcitation, initially localized in a phenyl ring of TDPO, may migrate into the C−C antibonding orbital without ever interacting with the nonbonding orbital on oxygen. Unfortunately, given the short (*ca.* 50 ns) lifetime of the *cis*-ylide and the low solubility of an electron deficient alkene such as fumaronitrile in cyclohexane, we are unable to trap the *cis*-ylide in cyclohexane and therefore are unable to measure the quantum yield for its production.

We were surprised to observe, in cyclohexane, the production of only one adduct, since fumaronitrile should be able to combine with the *trans*-ylide to form either adduct **1** or **3**. Our assignment to adduct **1**, based on its crystal structure,[19] of the stereochemistry shown in Scheme 1 agrees with literature precedent.[16,34−37] The literature assignments are based on an earlier NMR study[38] of phenyl-substituted pyrazolines which found that, in a five-membered ring, a proton *trans*-vicinal to a phenyl ring is more deshielded than one *cis*-vicinal to a phenyl ring. While applying NMR results for a five-membered ring with two heteroatoms conformationally restricted by a double bond to a five-membered ring with one heteroatom and no double bonds would appear tenuous, it does appear to hold.

We can argue in favor of steric factors for the production of adduct **1** in preference to adduct **3** in cyclohexane. In the transition state for 1,3-dipolarophilic addition, a *trans*-vicinal orientation of the bulky cyano groups to the bulky phenyl rings may be favored. However, photolysis in acetonitrile in the presence of fumaronitrile yields both adduct **1** and **3** in roughly equal yields, arguing in favor of ionic, rather than steric, control of these transition states.

We are currently measuring the quantum yields for photolysis of TDPO in polar solvents such as acetonitrile and 1-propanol in hopes of better understanding the role of solvent in this chemistry.

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Supporting Information Available: ^{1}H NMR spectra of adduct **1**, adduct **2**, and adduct **3** (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead for ordering information.

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