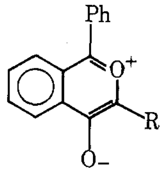
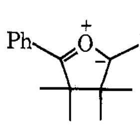
Photogeneration and Reactions of Acyclic Carbonyl Ylides[1]

Summary: The photoinduced formation of carbonyl ylides and their addition to dipolarophiles is illustrated with several typical precursors, including 3,3-dicyanostilbene oxide and related compounds, and the mechanism discussed.

Sir: Thermal as well as photochemical generation of azomethine ylides from aziridines has been studied extensively and the stereochemical predictions based on orbital symmetry considerations have been verified.[2] While the thermal formation of carbonyl ylides from oxiranes also has been investigated thoroughly,[3,4] studies of the photochemical counterpart of this process are complicated by the propensity of many oxiranes to undergo competitive [3 → 2 + 1] photocycloelimination to carbenes purportedly by way of carbonyl ylide intermediates. [5]Indirect evidence that such ylides are photolabile and do give carbenes upon irradiation has been presented;[6-8] however, to date the interception of photogenerated ylides has been limited to cyclic cases including **1a**,[9a] **1b**,[9b] and **2**,[9c] which are not disposed to form carbenes. This may be attributed to stabilizing features inherent in cyclic ylides, and/or efficient reversible ketocarbene formation. Intervention of reversible C–O bond cleavage could also occur. It should be noted that spectroscopic evidence for carbene formation could not be obtained with higher homologues of **2**.[7]



1a, R = Ph
b, R = CH_3



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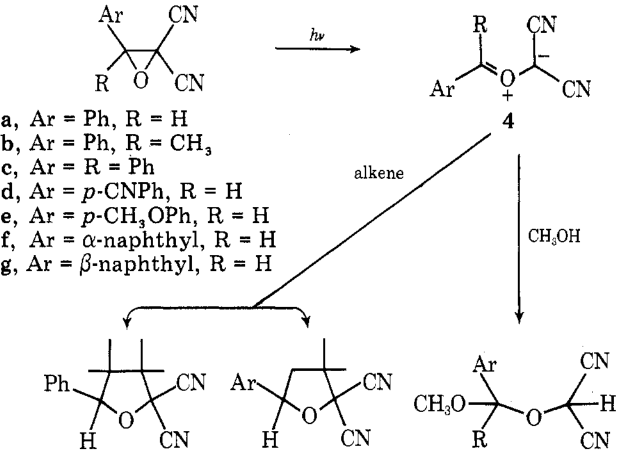
We have demonstrated that the photofragmentation of oxiranes is suppressed in the absence of vicinal diaryl substitution and this led to investigate the photochemistry of a series of dicyanooxiranes **3**.[6,7] The thermochemical properties of **3a**, **3b**, **3c**, and **3e**, as well as the related ethyl α-cyanophenylglycidates had been studied;[4] however, our recent investigations conducted at ambient and subambient temperatures have revealed some novel aspects of carbonyl ylide chemistry which are of mechanistic as well as synthetic significance.[1]



3a, Ar = Ph, R = H
b, Ar = Ph, R = CH_3
c, Ar = R = Ph
d, Ar = *p*-CNPh, R = H
e, Ar = *p*-CH_3OPh, R = H
f, Ar = α-naphthyl, R = H
g, Ar = β-naphthyl, R = H

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7a, Ar = Ph
b, Ar = *p*-CH_3OPh
c, Ar = α-naphthyl
d, Ar = β-naphthyl

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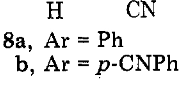

8a, Ar = Ph
b, Ar = *p*-CNPh

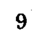

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Table I. Photocycloaddition of Oxiranes to Dipolarophiles

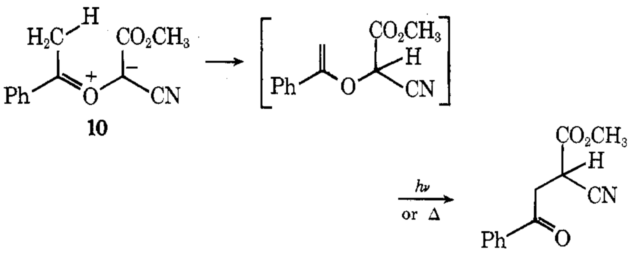
Oxirane[a]	Dipolarophile[b]	Irradiation time, hr	Product	% yield
3a	2,3-dimethyl-2-butene	6	**6**	51[c]
	Isobutylene	4	**7a**	90
	Ethylene	6	**8a**	84
	Acetylene	6	**9**	54
3d	Ethylene	6	**8b**	60
3e	Isobutylene	6	**7b**	34[c]
3f	Isobutylene	18	**7c**	78
3g	Isobutylene	6	**7d**	90

[a] Oxirane samples of 0.5–0.67 mmol were employed. [b] Degassed benzene solutions were saturated with the gaseous alkenes. [c] Aldehydes or oxetanes (~15–20%) were detectable by NMR.

The ylides **4a–e** may be generated by photolysis at 254 nm, while **4f** and **4g** form at 350 nm.[10] With the exception of **4d** all may be intercepted with protic solvents such as methanol with formation of the ketals or acetals **5**.[11] Precedent exists for cyclopropane photosolvolysis with C–C bond cleavage although further study is required to clarify the mechanism.[12] The adducts **5**, acetals or ketals of cyanohydrins, are unstable, but were characterized by NMR and hydrolyzed to the expected aldehydes or ketones.

The cycloaddition of ylides **4** (excluding **4b** and **4c**) generated photochemically from the oxiranes **3** to dipolarophiles also may be accomplished in solution at ambient or subambient temperatures. Efficient trapping may be achieved even with highly volatile dipolarophiles such as ethylene and acetylene to give **8** and **9**, respectively, and this provides a distinct synthetic advantage over thermal methods. Benzene was found to be one solvent of choice in such reactions. The [3 → 2 + 1] cycloelimination reactions are suppressed in benzene and the implications of this observation are discussed later. The oxiranes **3a** and **3d–g** give the corresponding cycloadducts in moderate to high yields. The conversion level is a function of the oxirane and dipolarophile structures (see Table I). Methyl α-cyano- and α-carbomethoxyphenylglycidates behave similarly in photocycloaddition reactions and will be the subject of a future communication.

In the case of **4b** photocycloadditions are circumvented and several dark intractable products are formed in low yield. From our experience with the carbomethoxy analogue **10**, where the photoreaction is cleaner, proton transfer occurs to give the enol ether which subsequently undergoes a [1,3]-sigmatropic shift to form methyl 2-cyano-3-benzoylpropionate (**11**). The structure of this product was confirmed by independent synthesis through base-catalyzed alkylation of phenacyl bromide with cyanoacetic ester. Furthermore, those factors which promote ylide stability and/or suppress cycloaddition allow for an increase in ylide steady-state concentration and concomitant absorption. For example, **4c** does



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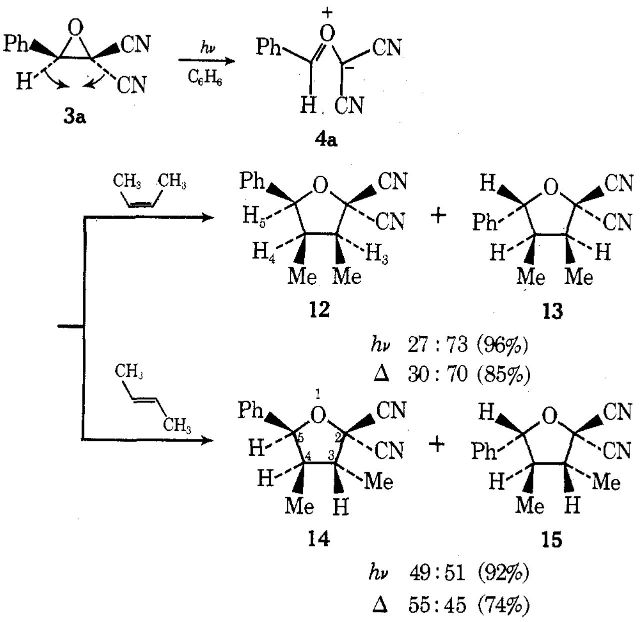
not undergo cycloaddition reactions which could be attributed to an increase in adverse steric interactions with methyl substituted alkenes and thus the probability of photocleavage is enhanced.[13]

The unusual activity displayed by benzene as a solvent suggested that the nature of the excited states implicated in the photoconversion of the oxiranes **3** to the ylides **4** should be investigated. While acetone (E_T = 79 kcal mol^{-1}) was found to be ineffective as a solvent sensitizer for **3a**, the formation of the ylide **4g** derived from the corresponding β-naphthyl analogue **3g** which gives the adduct **7d** is effectively sensitized (>90%) by benzophenone (E_T = 69 kcal mol^{-1}). More surprising is the fact that anthraquinone (E_T = 62 kcal mol^{-1}) is capable of sensitizing the formation of **4g** from **3g**, as evidenced by interception of the former with methanol or isobutylene. In the case of **3g** even a visible source is sufficient to achieve oxirane C–C single-bond cleavage to **4g** in the presence of anthraquinone. That triplet states of the sensitizers were effectively populated in these instances was demonstrated by utilization of uranyl glass and naphthalene filters to preclude direct oxirane excitation. We conclude from the data that ylide formation is at least in part a triplet process and that benzene behaves as a high energy (E_T = 84 kcal mol^{-1}) solvent sensitizer in the reactions described for **3a** and related oxiranes. *trans*-1,3-Pentadiene (E_T = 59 kcal mol^{-1}) was found to quench ylide formation with **3a** which is not unexpected in view of the magnitude of the triplet energy of this oxirane (i.e., 79–84 kcal mol^{-1}).

While the nascent ylides may be formed in their triplet states, the subsequent [3 + 2 → 5] cycloaddition reactions to dipolarophiles are regioselective and stereospecific. These are features which characterize the corresponding ground-state reactions and indicate that intersystem crossing to the singlet manifold occurs prior to cycloaddition.[3] In view of these results it is tempting to propose that the competitive [3 → 2 + 1] cycloelimination reactions of the oxiranes **3** to carbenes may occur from the singlet manifold. Thus the data accumulated do not preclude intervention of cheletropic and/or sequential components in which the excited singlet oxirane undergoes concerted and/or stepwise fragmentation to dicyanocarbene and the carbonyl component, perhaps with initial C–O bond cleavage.

Regioselective addition reactions of the photogenerated carbonyl ylides **4** to alkenes may be demonstrated by irradiation (254 nm)[10] of **3a** (0.5 mmol) in benzene saturated with isobutylene. The sole adduct is **7a** whose structure is evident from NMR data. The typical spin-coupling between methylene and benzyl protons as well as the absence of detectable shielding of either methyl group precludes the alternate regioisomer. Similar results were found with **4e** (254 nm)[10] as well as **4f** and **4g** (350 nm)[10] where the adducts formed with isobutylene are **7b, 7c,** and **7d,** respectively.

The stereospecific character of these reactions is evident from the results obtained upon addition of **4a** to either *cis*- or *trans*-2-butene in benzene. *cis*-2-Butene reacts with **4a** to give a pair of epimeric tetrahydrofurans (**12** and **13**) which differ from those (**14** and **15**) obtained when *trans*-2-butene is the dipolarophile. The isomeric structures of the photoproducts **12–15** were established from combustion analytical, ir, mass spectral, and NMR data. The presence of an NOE observed between H_3 and H_4 and their vicinal *cis*-methyl groups at C_4 and C_3, respectively, in **14** (10%) and **15** (10%), but not **12** and **13**, serves to differentiate the *trans*-dimethyl epimeric set **14** and **15** from their cis counterparts **12** and **13**.



hν 27 : 73 (96%)
Δ 30 : 70 (85%)

hν 49 : 51 (92%)
Δ 55 : 45 (74%)

In systems studied by Huisgen[3c] the magnitude of such vicinal ring coupling constants proved unreliable for stereochemical assignments in tetrahydrofurans bearing aryl groups at the 2 and 5 positions. We have observed that the trans coupling constants for **14** and **15** ($J_{3,4}$ = 11.0 and 11.5 Hz, respectively) are significantly higher than those for the cis isomers **12** and **13** ($J_{3,4}$ = 5.5 and 7.5 Hz, respectively) in a broad spectrum of adducts. Similar trends have been noted by Robert[4b] and Vandewalle[14] in related dicyanotetrahydrofurans and dimethylcyclopentanes, respectively. Thus it appears that coupling constant values can furnish reliable stereochemical information in such systems provided caution is exercized in cases where bulky substituents are present which might disrupt orientational factors responsible for the effect in conformationally mobile systems.

It should be noted that the adduct **13** is formed in higher yield from **4a** and *cis*-2-butene than the alternate epimer **12.** The magnitude of the difference is in accord with expectations based upon minimum steric interactions in the "two planes" orientation complex for the transition state leading to cycloaddition in the ground state.[3e,f] The results of the addition of **4a** to *trans*-2-butene are more difficult to assess since little significance may be attached to the apparent minor preference for the more stable adduct **15.** The relative amounts of the epimeric adducts (i.e., 12:13 and 14:15) are within experimental error of that obtained thermally at 120 °C which provides additional support for the contention that the cycloaddition reactions are ground-state processes.

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(11) A metastable ketal-enol ether formed by addition of ethanol to **1a** has been proposed as a rational intermediate in a mechanistic scheme leading to the ultimate isolable photoproducts obtained from this ylide in ethanol; however, this adduct was characterized solely by chemical transformations conducted without isolation in which ultraviolet spectroscopy served as the only analytical tool. See E. F. Ullman and W. A. Henderson, *J. Am. Chem. Soc.*, **88**, 4943 (1966).

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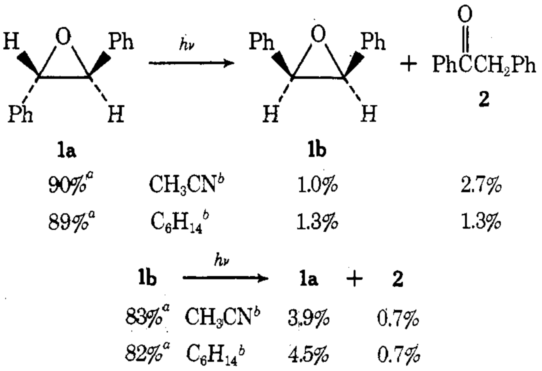
Photochemistry of *cis-* and *trans-*Stilbene Oxides

Summary: Stilbene oxides undergo photochemical ring opening from both singlet and triplet excited states to form carbonyl ylides which have been trapped with electron-deficient olefins; the resulting tetrahydrofuran adducts are formed stereoselectively in moderate yields from the singlet excited oxiranes, but are quantitatively obtained in a novel, synthetically useful fashion from triplet sensitized reaction mixtures.

Sir: The photochemistry of aryloxiranes has attracted considerable synthetic interest and mechanistic scrutiny within recent years.[1] *vic*-Diaryloxiranes have been observed to undergo photochemical [3 → 2 + 1] cycloelimination to produce synthetically useful yields of carbenes and carbonyl compounds.[1a,2] One of the interesting mechanistic features of these reactions is the apparently competitive fission of the oxirane C–C and C–O bond producing reactive intermediates which lead to the observed products.[3-5] Photochemical cleavage of the oxirane C–C bond produces carbonyl ylides which previously had been postulated[6] and more recently detected and characterized by spectroscopic means.[7] While the thermal ring opening of aryl oxiranes is well known to produce carbonyl ylides which were studied and trapped in subsequent 1,3-dipolar cycloaddition reactions,[8,9] the photochemically formed ylides have been less well characterized.[10,11] In the present paper, we wish to describe briefly data pertaining to the mechanistic aspects and synthetic utility of the photochemistry of the parent aryloxiranes, the *cis-* and *trans-*stilbene oxides.

Simultaneous irradiation[12] of the *trans-* and *cis-*stilbene oxide isomers in acetonitrile and in hexane with 2537-Å light at ambient temperature effects photoisomerization as outlined in Scheme I.[13]

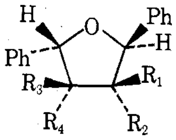
Scheme I



[a] Indicates amount of unconsumed starting material. [b] Solvent.

It is evident that *cis*-stilbene oxide photoisomerizes to its trans isomer, **1a**, much more readily than is observed for the reverse process, while the formation of deoxybenzoin (**2**) occurs ~6–7 times more readily from **1a** than from **1b**.

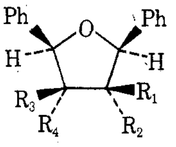
Examination of molecular models suggests that orientation of the phenyl π electrons relative to the C–C or C–O oxirane bond may control which products are preferentially formed. In **1a**, the absence of steric constraints permits aryl π overlap with the cleaving C–O σ bond leading to formation of deoxybenzoin. In **1b** this overlap is sterically hindered and instead aryl π overlap with the oxirane C–C bond appears favored, permitting facile cis–trans isomerization.[14] Similar arguments have been advanced previously to explain photochemical transformations of small-ring carbonyl compounds[15] and arylcyclopropanes.[16] Models also suggest a precedence for orbital participation in oxirane ring opening in the photolysis of 9,10-phenanthrene oxide reported by Griffin[17] and Chapman.[18]



3a, $R_1 = CO_2CH_3$; $R_2 = R_3 = R_4 = H$

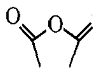
b, $R_2 = CO_2CH_3$; $R_1 = R_3 = R_4 = H$

c, $R_1 = R_3 =$  ; $R_2 = R_4 = H$



4a, $R_1 = CO_2CH_3$; $R_2 = R_3 = R_4 = H$

b, $R_2 = CO_2CH_3$; $R_1 = R_3 = R_4 = H$

c, $R_1 = R_3 =$  ; $R_2 = R_4 = H$

d, $R_2 = R_4 =$  ; $R_1 = R_3 = H$

When *trans-* or *cis-*stilbene oxide is irradiated directly with 2537-Å light in the presence of methyl acrylate or maleic anhydride, a product mixture containing previously observed photoproducts (vide supra),[1-4] as well as new tetrahydrofuran (THF) adducts **3** and **4**, was obtained. The yields of these adducts are given in Table I.[19] The photocycloaddition of stilbene oxides with electron-deficient olefins can be rationalized by the assumption that the electronically excited oxi-