Tetrahedron Vol. 37, No. 19, pp. 3345 to 3355, 1981
Printed in Great Britain.

0040-4020/81/193345-11$02.00/0
Pergamon Press Ltd

PHOTO- AND THERMOINDUCED GENERATION OF 1,3-DIARYL CARBONYL YLIDES FROM 2,3-DIARYLOXIRANES 1,3-DIPOLAR CYCLOADDITIONS TO DIPOLAROPHILES

J. P. K. Wong,[1a] A. A. Fahmi, G. W. Griffin,* and N. S. Bhacca
Department of Chemistry, University of New Orleans, New Orleans, LA 70122, U.S.A.

(*Received in USA April 1981*)

Abstract—A group of symmetrically substituted 2,3-diaryloxiranes have been studied as photoprecursors for carbonyl ylides. The stereochemistry of the adducts obtained upon interception of these 4n *pi*-transient systems with a variety of dipolarophiles provides information on the mode(s) of electrocyclic opening of the oxiranes to carbonyl ylides, as well as the mechanism of the 4n + 2 cycloaddition process. The stereochemistry of the dipolarophiles is preserved in the cycloadducts, which is consistent with a concerted addition process; however, solvent effects, steric hindrance, and possibly secondary orbital overlap factors all may play a role in determining the product distribution.

This study was initiated to assess the dominant forces underlying the ring-opening of oxiranes to carbonyl ylides. Evaluation of the constraints imposed by orbital topology on such conversions in a series of 2,3-diaryl oxiranes constituted a major impetus for this inquiry. Since dipolarophilic trapping proved essential, it was of paramount importance to establish the structures of a series of cycloadducts and confirm if, and under what conditions, these results might serve as reliable criteria for deducing the stereochemistry of the nascent carbonyl ylides implicated. The response of oxirane ring-opening and subsequent [4 + 2]-cycloadditions to steric variations, as well as the potential intervention of secondary overlap interactions constitute additional factors probed. The multiplicity of the nascent photogenerated carbonyl ylides and the electronic state(s) implicated in the cycloaddition reactions are subjects also addressed.

The three sets of *trans* and *cis* isomeric 2,3-diaryl substituted oxiranes displayed in Table 1, namely **1**, **2** and **3**, as well as *trans*- and *cis*-stilbene oxides (**4**) were synthesized and examined to evaluate the relative importance of factors which control the photogeneration of carbonyl ylides and their subsequent reactions. It should be noted that ylide formation from oxiranes is complicated by competitive processes, including (a) deoxygenation,[3] (b) hydrogen, alkyl or aryl migration,[4] and (c) cycloelimination.[5] Other groups have trapped photogenerated carbonyl ylides derived from selected oxiranes,[6-9] and their results will be described in context with our own work in the area.

Preparation of oxiranes

In order to prepare the independent pairs of alkene precursors for the stilbene oxides **1–4**, we resorted to three independent approaches. (*E*)-2,3-Dimethylstilbene (**5a**) was prepared by dehydration of 2,3-diphenyl-2-butanol. The latter was synthesized by addition of phenylmagnesium bromide to 3-phenyl-2-butanone, which in turn was obtained by C-alkylation of the enolate of phenylacetone with methyl iodide. Irradiation of **5a** in benzene provides a mixture of alkenes in which the *Z* isomer **5b** predominates (2:3), and when epoxidized with MCPBA affords the corresponding 2,3-dimethylstilbene oxides **1a** and **1b**, which are more easily separated by thick-layer or column chromatography than the precursor stilbenes **5a** and **5b**.

Table 1.

1a, $R_1 = R_4 = CH_3$; $R_2 = R_3 = Ph$
b: $R_1 = R_2 = CH_3$; $R_3 = R_4 = Ph$
2a: $R_1 = R_4 = CH_3$; $R_2 = R_3 = $ 2-Naph
b: $R_1 = R_2 = CH_3$; $R_3 = R_4 = $ 2-Naph
3a: $R_1 = R_4 = H$; $R_2 = R_3 = $ 2-Naph
b: $R_1 = R_2 = H$; $R_3 = R_4 = $ 2-Naph
4a: $R_1 = R_4 = H$; $R_2 = R_3 = Ph$
b: $R_1 = R_2 = H$; $R_3 = R_4 = Ph$

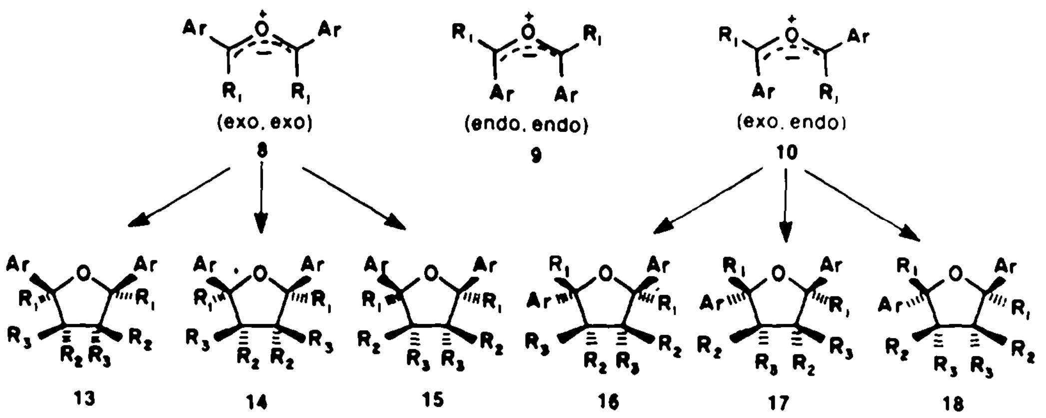
Reductive coupling of 2-acetonaphthone according to the McMurry method[10] gave a mixture of (*E*)- and (*Z*)-2,3-bis(2-naphthyl)-2-butenes, respectively, enriched in the latter. The *Z* isomer **6b** was separated from the *E* isomer **6a** by column chromatography and then oxidized with MCPBA to give the corresponding oxirane **2b**. The *E* isomer was obtainable by photoisomerization of the prepurified *Z* counterpart **6b** and oxidized in a similar fashion.

The two-phase Wittig procedure[11a] provided a superior route for synthesis of the alkenes **7a** and **7b**, which proved less readily accessible by other routes. The phosphonuim salt prepared from 2-bromomethylnaphthalene and subsequent treatment with triphenylphosphine was treated with sodium hydroxide to give the corresponding ylide. Condensation of this ylide with 2-naphthaldehyde afforded a mixture of **7a** and **7b** that was readily separated on the basis of solubility. These alkenes were then oxidized independently to the desired oxiranes **3a** and **3b**, respectively.

The *trans* and *cis* isomers of stilbene oxides (**4a** and **4b**, respectively) were synthesized by peroxidation of the corresponding stilbenes with MCPBA.[12]

Photoinitiated cycloadditions of **1** *and* **3** *to dipolarophiles*

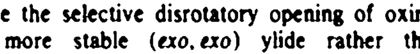
Three planar stereoisomeric carbonyl ylides of configurations designated (*exo, exo*), (*endo, endo*) or (*exo, endo*) (**8**, **9** and **10**, respectively) may be viewed as products of the electrocyclic opening of the 2,3-diaryloxiranes **1**, **2** and **3** (Scheme 1). Nonplanar "carbonyl ylides," including the 90°, 90° species (face to face) **11**



	Ar	R_1	R_2	R_3
(a)	Ph	CH_3	CN	H
(b)	Ph	CH_3		H
(c)	Ph	CH_3	CO_2CH_3	H
(d)	2-Naph	H	CO_2CH_3	H
(e)	2-Naph	H		H
(f)	2-Naph	H	CH_3	H
(g)	Ph	H	CO_2CH_3	H
(h)	Ph	H		H

Scheme 1.

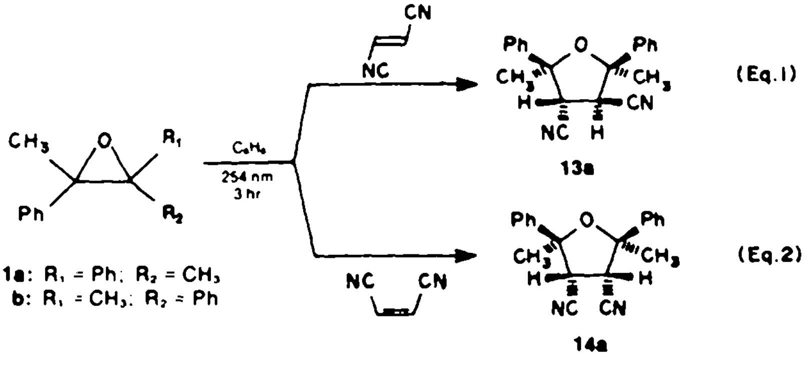
and the 0°, 90° conformation **12** are energetically unfavorable if calculations conducted on the opening of ethylene oxide are reliable in these systems.[13]



11 12

The formation of the planar (*endo, endo*) ylide **9** is sterically obstructed if the *endo* substituents are bulky. In such cases, thermodynamic factors override and dicate the selective disrotatory opening of oxiranes to the more stable (*exo, exo*) ylide rather than the (*endo, endo*) counterpart.[14] The latter then may be disregarded as active dipoles. Presumably, the cycloadditions of carbonyl ylides to dipolarophiles are thermally allowed 6 *pi*-electron processes, which proceed concertedly through a five center twoplanes orientation complex[14] to give tetrahydrofurans with maintenance of stereochemical integrity of the ylide and dipolarophile. Even if addition is accompanied by isomerization of the symmetric *E* and *Z* dipolarophiles, only three THF adducts **16**, **17** and **18** may be formed. A total of six isomeric THF adducts may then be anticipated if photoinduced opening does not occur stereospecifically and/or ylide equilibration to give a mixture of **8** and **10** is established subsequent to stereospecific opening.

The HOMO ylides derived from **1a** and **1b** undergo efficient [3 + 2 → 5]-photoinduced addition to electron deficient dipolarophiles like fumaro- and maleonitrile (eqns 1 and 2). In each case, the dipolarophiles maintain their stereochemical integrity during cycloaddition although the formation of the adducts **13a** and **14a** reveals that the same (*exo, exo*) ylide is implicated despite the fact that the precursors differ structurally. The absence of stereospecificity observed in the addition of the ylide(s) derived from **1a** may be explained in one or all of the following ways.



(1) The oxirane, a 4n *pi*-system, may open as anticipated (disrotatory) in the excited state giving the (*exo, endo*) ylide followed by rapid thermal and/or photoisomerization to give the thermodynamically more favored (*exo, exo*) ylide.

(2) As a result of adverse steric action, the magnitude of the thermodynamic instability may be sufficient to overcome the orbital topological control. Thus, photocleavage of **1a** may occur preferentially in a con fashion, contrary to expectations based on theory, to give the more stable (*exo, exo*) ylide.[14] It is conceivable that this mechanism is operative considering that oxirane opening adheres less stringently to theory than their aziridine counterparts in thermal processes described by Huisgen.[16]

(3) Initial photoinduced dis opening of **1a** followed by thermal recyclization in the allowed con fashion necessitates isomerization to **1b**. Subsequent photoinitiated dis reopening of **1b** would then explain generation of the more stable (*exo, exo*) ylide, but is probably of minor significance.

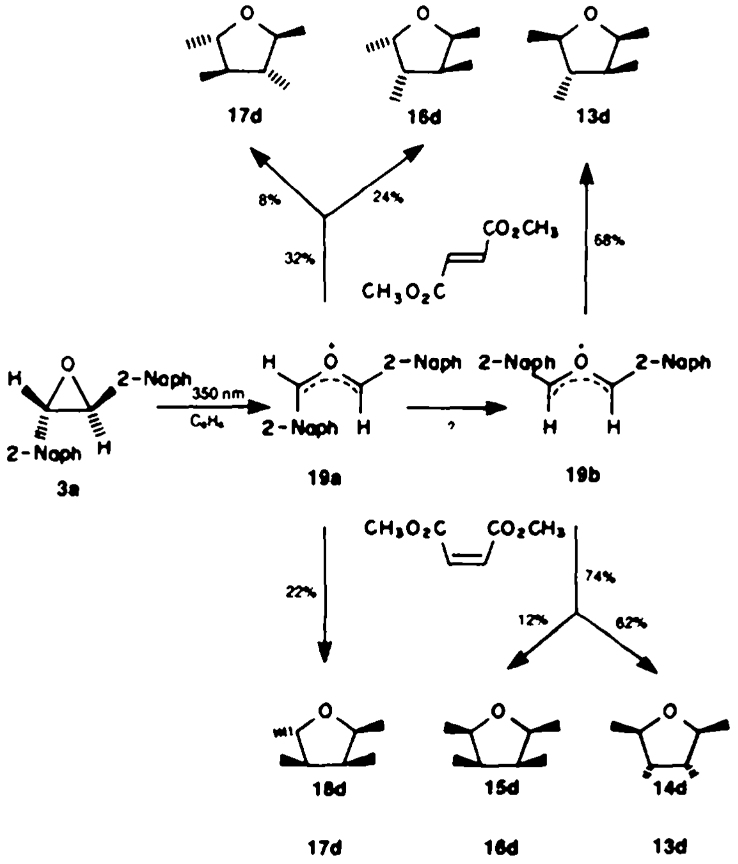
We found upon irradiation of **1a** and **1b** in a rigid matrix (77K)[17] that the spectra of the ylides formed from these oxiranes, unlike those from the stilbene oxides[18] are identical. Probably, the adverse effects embodied in endo aryl interactions thwart opening in the dis mode.

No addition is detected when the analogous 2,3-dinaphthyl oxiranes **2a** and **2b** are irradiated with electron deficient dipolarophiles, despite the fact that photolysis in a matrix of 2-methyltetrahydrofuran at 77K gives a green species attesting to the fact that ylide formation occurs. The selection of naphthyl substituents which absorb at longer wavelength was dictated by our desire to avoid concommitant photoisomerization of the dipolarophiles, which complicates product analysis.

Our inability to achieve cycloaddition of the isomeric 2,3-dimethyl-2,3-dinaphthyl oxiranes was puzzling since positive results were obtained with the corresponding diphenyl analogs **1**. We assume that the failure of ylides derived from oxiranes **2** to undergo cycloaddition is a consequence of adverse steric interactions which develop in the two-planes complex and/or more efficient intersystem crossing to the triplet state (naphthalene $\phi = \sim 0.70$).[19b] To insure that the anticipated reactions were not subverted in an unexpected manner by triplet interconversion, we also studied the unsubstituted analogs, i.e. the isomeric 2,3-dinaphthyloxiranes (**3a** and **3b**).

In contrast, the ylides generated photochemically from the 2,3-dinaphthyloxirane **3a**, like those formed from **1a**, are intercepted by dipolarophiles [e.g. dimethyl maleate and fumarate (Scheme 2)], which failed to react with ylides derived from **2a** and **2b**. Our decision to use dimethyl maleate and fumerate as dipolarophiles rather than the corresponding nitrile employed with **1a** and **1b** was dictated by our interest to appraise stereochemical and secondary orbital overlap factors. Furthermore, the OMe substituents provide NMR signals which serve as convenient probes of adduct stereochemistry.

For expediency, we will first address the problem of the degree of stereorandomization of the dipolarophile at low conversations. Our discussion of partitioning of the



Scheme 2.

oxirane **3a** to isomeric ylides during or after electrocyclic opening prior to addition will be reserved until later.

The stereointegrity of dimethyl fumarate is preserved during formation of adducts **13d**, **16d** and **17d**, while that of dimethyl maleate is lost (Scheme 2). Control experiments preclude photoisomerization of **14d**, **15d** and **18d** as a source of adducts **13d**, **16d** and **17d**. Irradiations utilizing naphthalene as a sensitizer ($E_t = 60$ kcal/mol)[19c] confirm that sensitized interconversion of dimethyl maleate to fumarate (perhaps induced by the oxirane **3** itself) provides a reasonable explanation for the appearance of isomeric adducts **13d**, **16d** and **17d**. That these arise by addition of ylides **19a** and **19b** to dimethyl fumarate formed by sensitized photoisomerization of maleate is plausible considering the fact that the ratio of **13d**, **16d** and **17d** parallels that which was observed with dimethyl fumarate.

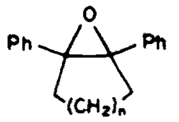
The relative rate of addition of the ylides **19a** and **19b** to dimethyl fumarate is qualitatively faster than to dimethyl maleate.[20] Such increased cycloaddition efficiency magnifies the contribution of the fumarate adducts to the overall product composition. Conversely, the lower reactivity of dimethyl maleate precludes detection of [4+2]-adducts formed at low level by sensitized isomerization.

The relative percentage of "non-stereospecific adducts" increase as the irradiation time is extended, i.e. the anti dicarbomethoxy adduct concentration (**13d**, **16d** and **17d**) exceeds that of the corresponding *syn* isomers after 72 hr. This finding may be accommodated by the mechanism proposed if it is assumed that the rate of isomerization of dimethyl maleate to fumarate competes with electrocyclic opening and cycloaddition and the relative reactivities of these dipolarophiles with **19a** and **19b** is considered. Clearly, our failure to achieve cycloadditions with **2** cannot be attributed to unfavorable or competitive photophysical processes caused by the presence of naphthyl substituents in view of the positive results obtained with **3a**.

Since we anticipate opening of **3b** in the dis mode in the excited state, the most stable ylide configuration (*exo, exo*) should be formed to the exclusion of the (*endo, endo*) or (*exo, endo*) alternatives. Thus, less stereorandomization might be expected during opening of **3b** relative to the trans isomer **3a**. Contrary to expectations, however, the product ratios from **3b** and dimethyl fumarate are identical to those obtained from **3a**, and this holds true for **3b** and dimethyl maleate in which **13d**, **16d** and **17d** are minor by-products. These results agree with the findings of Lee[6a] for *sensitized* cycloadditions of photogenerated ylides from stilbene oxides **4a** and **4b** and reveal that the precursor oxiranes, regardless of stereochemistry, open to a common set of ylides or ylide equilibration precedes cycloaddition.

Although the data presented discount a stepwise addition mechanism for the formation of **13d**, **16d** and **17d** from dimethyl maleate and **3a** and **3b**, we desired to exclude prior dipolarophile isomerization. To do so, we screened a series of alkenes, including (*Z*)- and (*E*)-2-butenes whose triplet states are sufficiently high ($Et \sim 80$ kcal) to avoid exothermic energy transfer from naphthalene ($E_t = 60$ kcal).[19c]

We recognized that this variation in dipolarophile structure could prove unrewarding since ylides derived from 2,3-diaryloxiranes generally give HOMO dipoles and react most efficiently with electron deficient dipolarophiles, according to the precepts of frontier orbital theory.[21] Our inability to trap cyclic ylides from **20a** and **20b**,[2] as well as 1,3-diaryl acyclic counterparts[5] with electron-rich dipolarophiles validates the widely applicable and accepted theory. Lee also recognized that the isomeric stilbene oxides,[6a] as well as chalcone oxides,[6b] fail to give adducts with electron-rich dipolarophiles.



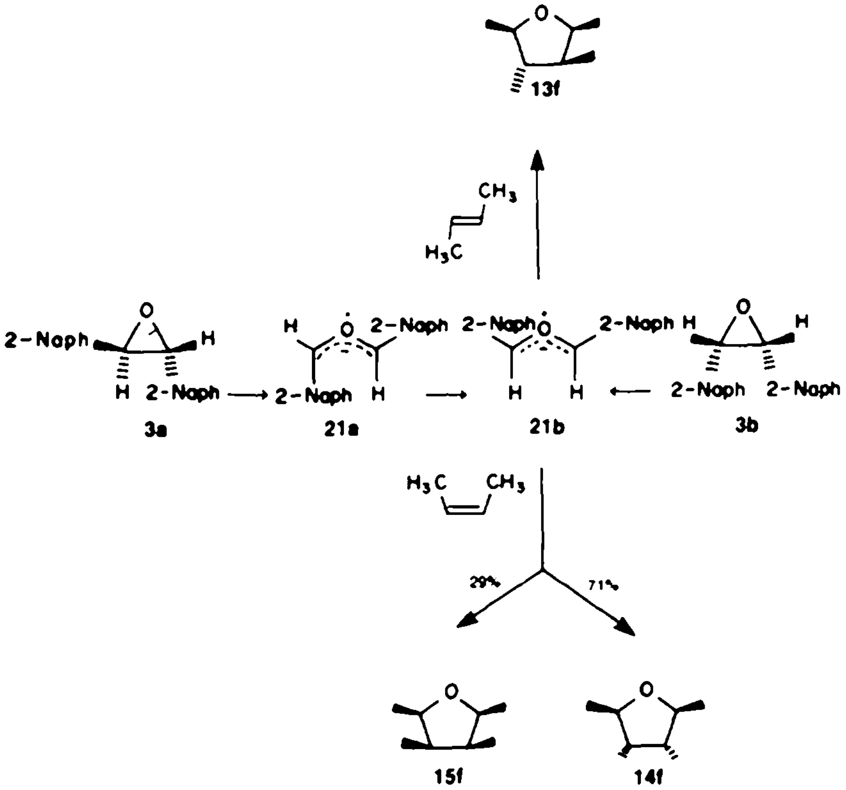
20a: n = 1
b: n = 2

Surprisingly, the illumination of **3a** and **3b** in the presence of (*E*)- or (*Z*)-2-butene provides tetrahydrofuran adducts (Scheme 3), although by-products derived from [3→2+1]-cycloelimination are also detected. The stereochemistry of the isomeric butenes is preserved in the [3+2]-cycloadducts; however, the structures of the cycloadducts **13f**–**15f** reveals that a single ylide of (*exo, exo*) configuration **21b** is implicated in the addition, which we attribute to the reduced reactivities of alkenes as dipolarophiles. Consequently, equilibration, if highly biased, could preclude trapping of all but the most stable dipole **21b**. Furthermore, enhanced intrinsic reactivity may be associated with the HOMO ylide **21b**, which is only manifested in greater selectivity with dipolarophiles of low reactivity, e.g. the 2-butenes.[21] In any event, the complexity of the tetrahydrofuran product mixtures is significantly reduced with respect to those obtained with more reactive dipolarophiles. A common ylide **21b** is intercepted from either **3a** or **3b**, which reacts with (*E*)-2-butene to give the sole adduct **13f**, and with (*Z*)-2-butene to give only **14b** and **15b** (Scheme 3), see dimethyl furmarate and maleate (Scheme 2), where three and six different adducts are formed, respectively.

Ylides derived from the isomeric stilbene oxides (**4a** and **4b**), it is reported,[6a] fail to undergo addition to norbornene; however, our success in achieving addition of the photogenerated (*exo, exo*) ylide **21b** to the isomeric 2-butenes led us to reevaluate the reaction with **4a** and **4b**. We, too, detected no evidence for the presence of cycloadducts of the type obtained from **21a** and **21b** with 2-butenes among the photoproducts of norbornene and **4a** or **4b**. Evidently, the 2,3-dinaphthyl oxiranes **3a** and **3b** do not constitute typical oxirane precursors for HOMO ylides and represent the first pair of unsubstituted diaryloxiranes which add to electron-rich dipolarophiles. Conjugating groups have a propensity for compressing frontier orbital energies of ylides. This could result in stabilization of the LUMO of **19b** to such an extent that its LUMO character is enhanced relative to that of the ylides derived from stilbene oxides.

The experimental details, normalized relative adduct ratios and typical yields utilized and/or obtained in the course of our studies of the cycloadditions of oxiranes to dipolarophiles under direct irradiation conditions are summarized in Table 2.

The multiplicity of nascent photogenerated ylides from **3a** and **3b** was probed using acetophenone as a triplet sensitizer. Uranyl glass coupled with a naphthalene solution served as a filter to preclude direct excitation of the oxiranes **3**. The relative ratios, as well as the yields of the adducts **13d**, **16d** and **17d** obtained are similar to that produced upon direct irradiation. Presumably, a common triplet species is formed in the sensitized and unsen-



Scheme 3.

Table 2. Direct photolysis of oxiranes in the presence of dipolarophiles

Entry	Oxirane (100 mg)	Dipolarophile[a] (10 equiv)	Solvent[c] (10 ml)	Lamp (nm) and Filter[e]	Irradiation Time, hr.	Relative Adduct Ratios, %[f] 13	16	17	18	14	15	Total Yield, %[g]
1	2a	FN	B	254 Q	5	(a) 100						35
2	2b	FN	B	254 Q	3	(a) 100						45
3	2a	MN	B	254 Q	5					(a) 100		30
4	2b	MN	B	254 Q	5					(a) 100		38
5	2a	MA	A	254 Q	6					(b) 47	53	30
6	3a	DF	B	350 U	0.5	(d) 68.4	23.6	8.0				44
7	3b	DF	B	350 U	0.5	(d) 68.8	22.5	8.7				48
8	3a	DM	B	350 U	0.5	(d) 3.1	1.0	0.4	21.5	61.8	11.9	47
9	3b	DM	B	350 U	0.5	(d) 2.5	0.9	0.3	21.2	63.3	11.8	42
10	3a	DF	A	350 U	0.5	(d) 78.8	15.9	5.3				28
11	3b	DF	A	350 U	0.5	(d) 76.3	17.5	6.2				33
12	3a	DM	A	350 U	0.5	(d) 9.2	2.2	0.7	12.1	45.5	30.5	32
13	3b	DM	A	350 U	0.5	(d) 9.4	1.9	0.6	12.4	44.8	30.9	27
14	3b	MA	A	350 U	6				(e) 4	39	57	24
15	3a	TB[b]	B[d]	350 P	12	(f) 100						29
16	3b	TB[b]	B[d]	350 P	12	(f) 100						31
17	3a	CB[b]	B[d]	350 P	12					(f) 71	29	24
18	3b	CB[b]	B[d]	350 P	12					(f) 72	28	26
19	2a or 2b	FN/MA	B	350 P	8	Not detectable						

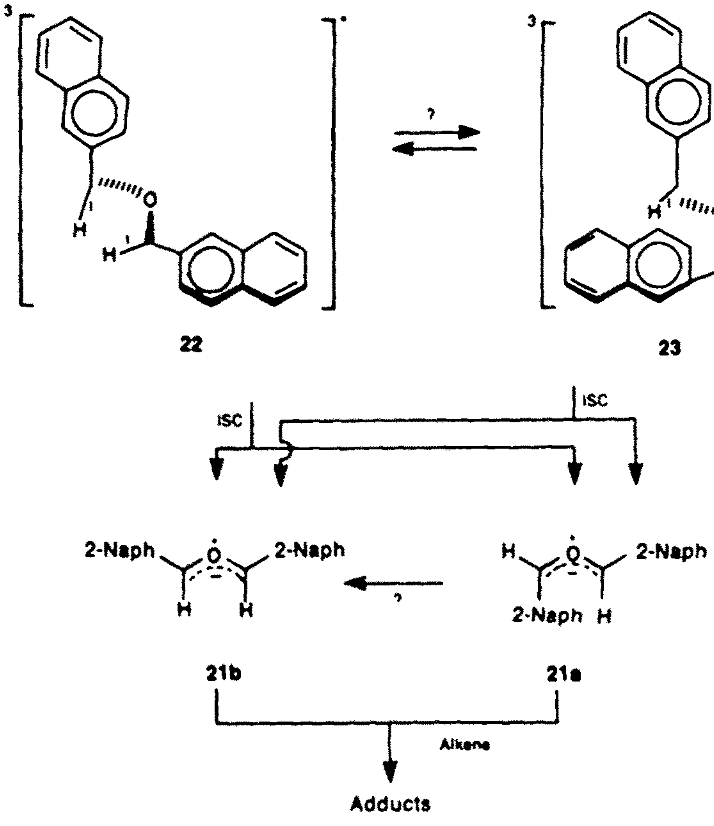
[a] FN=fumaronitrile, MN=Malconitrile, DF=dimethyl fumarate, DM=dimethyl maleate, MA=maleic anhydride, TB=(E)-2-butene, CB=(Z)-2-butene. [b] 5mL of the butene were used. [c] B=benzene, A=acetonitrile, [d] 5mL of solvent were used. [e] Q=quartz, U=uranyl, P=pyrex. [f] The relative ratios were determined by NMR (200 MHz when two or more adducts were present otherwise 60 MHz NMR was used) from the crude photolysates (except in entries 9, 10, 13 and 14) at low conversions, as indicated by the length of irradiation. The relative ratios of the adducts 13d, 16d and 17d (with trans ester substituents) in entries 9, 10, 13 and 14 were determined after they were separated together by TLC from the remaining three adducts whose relative abundance could be determined directly from the crude photolysates. In entries 5 and 14, the ratios correspond to that of the diesters obtained after subjecting the anhydride adducts to base hydrolysis and subsequent esterification with diazomethane. [g] The yields were determined after separation (TLC) of the adducts obtained at high conversions, *i.e.*, after all the oxiranes had been consumed, which may take as long as 10 days.

sitized cases prior to addition. Conceivably, the triplet intermediate(s) have orthogonal (0°, 90°) conformations, represented by **22** and **23**, which decay prior to addition to a common ratio of (*exo, exo*) and (*exo, endo*) planar ground state ylides **21a** and **21b** (Scheme 4).

We infer that additions of ylides derived from **3a** and **3b** to alkenes proceed with high stereospecificity (~99%), consistent with a concerted mechanism. This is true even when dipolarophile reactivity is low, e.g., the isomeric 2-butenes.

Thermally induced cycloadditions of the isomeric oxiranes 3 and 4 to dimethyl fumarate and maleate

In order to discern whether the photoadditions of the isomeric dinaphthyl oxiranes **3** occur in an excited or ground state process, thermolysis of the oxiranes in the presence of dipolarophiles was performed over a range of temperatures. Attempts to achieve thermal additions of **3a** and **3b** to 2-butenes, however, have escaped success. To date, we have been unable to contain these reaction mixtures in sealed ampoules at sufficiently high temperatures to achieve addition, and reproducible explosions have ensued during repeated attempts; however, thermal additions involving such oxiranes have been achieved with electron-deficient dipolarophiles (Table 3, entries 1–4). Unfortunately, dimethyl maleate is subject to isomerization at a temperature near 165°, and thus it is not possible to establish the addition stereochemistry; however, a comparison of the ratio of the two adducts **14d** and **15d** obtained thermally (5.2:1, Table 3) with that produced by photoinduced cycloaddition (5.2:1, Table 2, entries 8 and 9) lends further credence to



Scheme 4.

Table 3. Thermal induced cycloadditions of oxiranes and dipolarophiles

Entry	Oxirane (100 mg)	Dipolarophile[a] (50 equiv.)	Solvent[b] (0.5 ml)	Temperature and Time	Relative Adduct Ratios, %[c] 13	14	15	Total Adduct Yield, %[d]
1	3a	DF	B		(d) 100			37
2	3b	DF	B	170–185°C	(d) 100			44
3	3a	DM	B	6h	(d) 9	76	15	26
4	3b	DM	B		(d) 12	74	14	18
5	4a	DF	A		(g) 100			33
6	4b	DF	A	200–215°C	(g) 100			29
7	4a	DM	A	6h	(g) 34	61	5	27
8	4b	DM	A		(g) 87	12	1	12

[a] DF=dimethyl fumarate, DM=dimethyl maleate. [b] B=benzene, A=acetonitrile. Additions can also be achieved in the absence of solvent. [c] The ratios were determined by 90 MHz NMR. [d] The yields are not optimized and were determined after separation (TLC) of the adducts obtained at high conversions. It appears that the yields are a function of temperature and pressure, for example, by heating neat 3b and dimethylfumarate at 200°C for 3 days, over 70% of the adduct was isolated.

the postulate that even if the photogenerated ylide is formed in the excited state, decay to the ground state must occur prior to addition.[7,24] The necessary control experiments were performed to insure that the adducts **14d** and **15d** are stable under the reaction conditions.

It may be seen from the data displayed in Table 3 that thermoinduced cycloaddition reactions of **3** with dimethyl fumarate gives adduct **13d** as the sole product formed regardless of the stereochemistry of the precursor oxirane. The absence of **16d** and **17d**, which are thermally stable within the range, 170–185°, among the products from **3b** is conspicuous. The "allowed" conrotatory opening of **3b**, if operative, should generate the (*exo,endo*) ylide, which, upon interception by dimethyl fumarate, would give these adducts. Thus, it may be concluded that thermal isomerization of the ylide must precede cycloaddition, if indeed orbital symmetry constraints do exert control on the oxirane opening, i.e. opening to the (*exo,endo*) ylide followed by rapid isomerization to the (*exo,exo*) form, would not be detected if addition is relatively slow by comparison.

We have also achieved the thermoinduced cycloadditions of *trans*- and *cis*-stilbene oxides **4a** and **4b** to dimethyl maleate and fumarate. The results are similar to those obtained with the naphthyl analogs, except higher temperatures are required in the former case (Table 3, entries 5–8). This is not unexpected since the 2-naphthyl substituents are perhaps better able to stabilize the ylide than the corresponding phenyl substituents.

A comparison of the adducts generated by addition of the *cis*- and *trans*-stilbene oxides to dimethyl maleate at 200–215° reveals that the relative amount of the adduct **13g** is substantially higher when the oxirane has the syn configuration. This inducates that the activation energy for ring-opening of the *cis* oxirane is higher than that for the *trans* isomer, which is consonant with orbital symmetry postulates. Huisgen found that the activation energy for ring-cleavage of *cis* α-cyanostilbene oxide is 4 kcal higher than that of the *trans* isomer.[20] Under prolonged heating at elevated temperatures (220–235°), the isomeric stilbene oxide pairs of oxiranes give rise to the same reaction mixture with dimethyl maleate in which **13g** and **14g** are formed in equal quantity, while **15g**, the least stable member of the three possible adducts, is present in trace amounts. Clearly, thermoinduced isomerization has occurred; however, the adducts **13g**–**15g** are stable at lower temperatures (200–215°). In fact, the ratio of the two adducts **14g** and **15g** (12:1) obtained from either *trans*- or *cis*-stilbene oxide at 200° is identical to that obtained *via* electron transfer sensitization.

Electron transfer sensitized cycloadditions of 1 *and* 4 *to dipolarophiles*

Recently, Arnold and Albini[25] have shown that the photoinduced electron transfer reactions of *cis*- and *trans*-stilbene oxides (**4a** and **4b**, respectively) lead to C–C bond cleavage of the oxirane ring to give a radical cation. It is proposed that formation of the corresponding carbonyl ylide then occurs by back donation of an electron from the radical anion produced concomitantly with the radical cation. Dipolarophiles such as fumaro- and maleonitrile, as well as acrylonitrile, were employed. This discovery prompted us to examine the utility of this method with *trans*- and *cis*-2,3-dimethylstilbene oxides **1a** and **1b**, respectively. Indeed, we found that 1,4-dicyanonaphthalene proved to be an effective electron transfer sensitizer for inducing C–C bond cleavage in **1a** and **1b**, and the interception of the resulting (*exo,exo*) carbonyl ylide was readily achieved with maleo- and fumaronitriles (Table 4, entries 5–8). No cycloaddition was observed in the absence of DCN, thus confirming that excitation of this dinitrile is required to achieve these conversions.

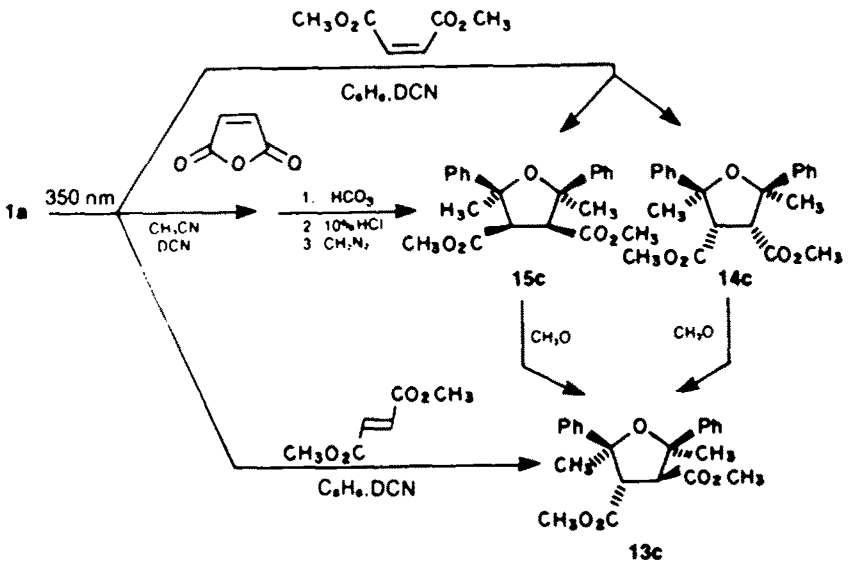
Additions of **1a** to maleic anhydride and dimethyl fumarate using DCN as a sensitizer give high yields of adducts (Scheme 5), although less efficiently. Esters **14c** and **15c** must be obtained directly from adducts **1a** and maleic anhydride, since they are not formed through direct addition of **1a** to dimethyl maleate. In contrast, however, addition to dimethyl fumarate does give rise to **13c**. The adduct **13c** is thermodynamically more stable than **14c** or **15c**, as evidenced by the fact that these esters may be epimerized to **13c**. The inefficiency of dimethyl maleate as a trapping agent may reflect the adverse steric interactions inherent in **13c**. Conceivably, the inability of this dipolarophile to achieve planarity may preclude favorable approach in the transition state.

In order to assess the role of secondary orbital effects in ylide cycloaddition reactions, DCN was used as sen-

Table 4. Cycloadditions of oxiranes and dipolarophiles via electron transfer sensitization[a]

Entry	Oxirane (100 mg)	Dipolarophile[b] (10 equiv)	Solvent[c] (10 ml)	Filter[d]	Irradiation Time, h	13	16	17	18	14	15	Total Adduct Yield, %
1	4a	DF	A	U	0.5	(g) 59.6	25.8	14.6				92
2	4b	DF	A	U	0.5	(g) 81.4	11.2	7.4				88
3	4a	DM	A	U	0.5				(g) 19.2	74.3	6.5	83
4	4b	DM	A	U	0.5				(g) 8.7	84.0	7.3	84
5	1a	FN	B	P	24	(a) 100						70
6	1b	FN	B	P	24	(a) 100						76
7	1a	MN	B	P	24					(a) 100		67
8	1b	MN	B	P	24					(a) 100		74
9	1a	MA	A	U or P	120					(b) 45	55	51[g]
10	1a	MA	B	U or P	120					(b) 91	9	81[g]
11	1a	DF	B	U	3	(c) 100						68
12	1a	DM	B	U	3				(c) none			

[a] 350nm was used, 1,4-dicyanonaphthalene (DCN) was the sensitizer. [b] DF=dimethyl fumarate, DM=dimethyl maleate, FN=fumaronitrile, MN=maleonitrile, MA=maleic anhydride. [c] A=acetonitrile, B=benzene. [d] U=uranyl, P=pyrex. [e] The ratios were determined by 200 MHz NMR when more than two adducts were present, otherwise 60 MHz NMR was used. In entries 9 and 10, the ratios correspond to that of the diesters obtained after subjecting the anhydride adducts to base hydrolysis and subsequent esterification with diazomethane. [g] Isolated as the diesters. In entry 9, 15% of acetophenone was detected, but only trace was present in entry 10.



Scheme 5.

sitizer to obtain the total spectrum of adducts of **4a** and **4b** with dimethyl fumarate and maleate (Table 4, entries 1–4), including the additional **16g**, **17g** and **18g**, which incorporate transaryl groups. These adducts are not formed thermally since thermal isomerization to the more stable (*exo*, *exo*) ylide probably occurs before addition. The availability of a complete set of adducts of known stereochemistry proved advantageous in subsequent NMR analytical studies of thermal and photoreactions conducted.

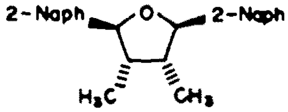
The ratio of adducts (**14g**:**15g**) was found to be 11.5:1 in these electron transfer reactions. This value is comparable to that obtained in the thermally induced cycloadditions (12:1, Table 3). This suggests that the transient intermediate formed with DCN, not unexpectedly, is in the ground state upon addition.

The solvent effects on product distributions for the electron transfer sensitization reactions are dramatic. For example, the DCN sensitized cycloaddition of **1a** to maleic anhydride in acetonitrile gives **14b** and **15b** in approximately equal amounts. When benzene is used as the solvent, the former adduct predominates almost to the exclusion of the latter (Table 4, entry 10). The adduct distribution may also be compared to that obtained upon direct irradiation, and it was found that in acetonitrile, the adduct distribution is identical (Table 2, entry 5); however, the adduct yield is enhanced in the sensitized process, presumably because the rate of fragmentation of oxirane to acetophenone is reduced since the O–O band for **1a** is at $\lambda < 275$ nm, which precludes excitation of the oxirane with the source used. The presence of acetophenone among the electron-transfer sensitized products is perplexing since Arnold and Albini observed no such fragmentation occurring during cycloadditions of stilbene oxides to fumaro- and maleonitrile.[25]

Factors responsible for the stereochemical course of cycloaddition

The relative ratio of ylide conformers and the cycloaddition stereochemistry is responsive to steric, electronic, as well as solvent effects. The sensitivity of ylide cycloadditions to steric effects is a characteristic noted in our laboratories, as well as by previous investigators,[24-26] and supported by the observations that large negative activation volumes are associated at least with thermal $[3+2 \rightarrow 5]$-cycloaddition reactions.[27] It is clear that steric hindrance to approach embodied in the dipolarophiles exerts a significant role in controlling the cycloaddition course. This is illustrated by the fact that in the electron transfer, sensitized additions of *trans*-2,3-dimethylstilbene oxide (**1a**) does not add to dimethyl maleate to form **14c** or **15c** or other adducts; however, this dipole adds to dimethyl fumarate to form **13c**, which on steric grounds is clearly the most stable of the three possible adducts.

The thermodynamically more stable adduct **14f** is formed in preference to the alternate cis dimethyl adduct **15f** when the ylides derived photochemically from *cis*- or *trans*-2,3-bis(2-naphthyl)oxirane adds to (*Z*)-2-butene (the ratio **14f**/**15f** = 2.5). This result is consistent with the "two-planes orientation complex" proposed by Huisgen as the encounter mechanism for the cycloaddition of ylides to dipolarophiles.[14] This concept also provides a rationale for the formation of **14a** to the exclusion of **15a** in the photoinduced (direct or electron transfer sensitized) cycloadditions of *trans*- and *cis*-2,3-dimethylstilbene oxides to maleontrile. Secondary orbital interactions between the aryl substituents and nitrile groups apparently exerts no control over the stereochemical course of the cycloaddition in this case; however, due to the linear character of the nitrile substituents, which



14f

15f

might have been anticipated. That the transition state leading to **14a** is less hindered than the counterpart for **15a** is not based solely on speculation and experimental data may be cited as evidence that a phenyl group is sterically more demanding than a methyl substituent.[28]

In contrast, secondary orbital interactions may be significant in cycloaddition reactions where dimethyl fumarate is involved as a dipolarophile. By way of review, the (*exo, endo*) ylides derived from the 2,3-bis(2-naphthyl) oxiranes (**3**) or stilbene oxides (**4**) add to dimethyl fumarate to give two adducts, of which one, in each case, is thermodynamically more stable. The same is true for the addition of the (*exo, exo*) ylide to dimethyl maleate. Our data indicate that in the former case, the more hindered adducts predominate, which is consistent with the principle of maximum accumulation of unsaturation (Alder Rule). In contrast, the reverse is true in the latter case. Such results were observed in the direct photolysis of **3** (Table 2, entries 6–13), and in the electron transfer sensitized reactions of **4** (Table IV, entries 1–4), as well as the thermal additions of these two pairs of oxiranes to dimethyl maleate (Table 3, entries 3, 4, 7 and 8). For example, the thermodynamically less stable adduct **16d** is formed preferentially relative to **17d** (2.8:1) in the photoinduced addition of dinaphthyl oxiranes **3** to dimethyl fumarate in benzene as the solvent (Table 2, entries 6 and 7). When dimethyl maleate is employed as the dipolarophile (Table 2, entries 8 and 9), the reverse effect is observed, i.e. **14d** is more abundant than **15d** (5.3:1). We propose that in those cases where dimethyl maleate is the dipolarophile, planarity cannot be achieved due to steric factors. Thus, the *pi*-orbitals of the resulting skewed partner in the "two-planes orientation complex" cannot overlap as effectively, relative to fumarate, with the *pi*-orbitals of the ylide.

The ratio of the adducts **16d** and **17d** (2.9) in the additions of the (*exo, endo*) dinaphthyl ylide **10** to dimethyl fumarate (Table 2, entries 10 and 11) is greater than that observed when naphthyl is replaced by phenyl (**16g**/**17g** = 1.7) (Table 4, entries 1 and 2). Such an enhancement would be anticipated if electronic interactions are operative since the *pi*-electron cloud is more extensively delocalized in the naphthyl than the phenyl substituents. This conceivably permits more extensive overlap in the orientation complex.

Solvent affects the product distribution in two ways. First, polar solvent (acetonitrile) enhances the secondary intermediates or relaxes steric restrictions. In other words, the formation of endo adducts is formed. Such solvent effects are in accord with the findings of Berson and Steinwetz,[29] and their respective co-workers, among others. Secondly, acetonitrile favors the formation of the (*exo, exo*) ylide to the (*exo, endo*) counerpart, i.e. in acetonitrile, a higher percentage of THF's is formed, which incorporate cis aryl substituents. These data reaffirm that of Lee obtained in the sensitized cycloadditions of the isomeric stilbene oxides to methyl acrylate.[6a] Furthermore, the overall adduct yield was enhanced when benzene is used as a solvent.[30]

Structural and stereochemical assignments of new tetrahydrofurans

The stereochemical assignments, neglecting chirality, required for the twenty tetrahydrofurans formed during this study from three of the four isomeric pairs of **1**, **3** and **4** were assigned unequivocally on the basis of (1) the shielding effect of aryl substituents on *syn* vicinal protons, (2) independent syntheses using maleic anhydride adducts as precursors for *syn*- and *anti-cis* diesters, and (3) the results of base catalysed isomerizations. The structural assignments in all cases are self-consistent in the sense that all isomers isolated in each series conform to spectral, analytical and thermodynamic expectations. Satisfactory elemental analyses and mass spectra, of course, were obtained on all adducts, and those derived from **3** and **4** exhibit the characteristic AA'BB'NMR pattern. We have also confirmed, in agreement with Huisgen,[11a] that NMR coupling constants for C_3H–C_4H do not serve as reliable criteria of stereochemistry in these non-rigid tetrahydrofuran series, and such data must be interpreted with caution. However, it is well documented that protons of a methyl or methoxy substituent syn to an aryl group on a 5-membered ring are shielded relative to those of the anti epimer. This has proven to be a reliable criterion for assigning stereochemistry in a variety of such systems.[11] Indeed, the NMR signals of the shielded syn methyl substituents in twelve of the new tetrahydrofurans synthesized during the course of this study are approximately 0.5 ppm upfield from their unshielded counterparts, in which the methyl group is anti to the aryl nucleus. Details of the complete structural elucidation of all adducts and their spectral characteristics will constitute the subject of a subsequent paper in this area.

EXPERIMENTAL

General. UV and visible spectra were obtained on a Cary Model 17 spectrophotometer. Infrared spectra were recorded on either a Perkin–Elmer 257 or 283 spectrophotometer. Mass spectra were determined with a Hitachi Perkin-Elmer RMU-6E spectrometer.

The 60 MHz PMR spectra were obtained on a Varian A-60 or Hitachi Perkin–Elmer R-20B spectrometer. The 90 MHz spectra were determined with a Jeol FX-900 spectrometer, while the 200 MHz spectra were recorded on a Bruker 200 MHz spectrometer through the courtesy of Prof. N. S. Bhacca (Louisiana State University, Baton Rouge, Louisiana). M.ps are uncorrected, and satisfactory combustion analyses were obtained on all new compounds.

Preparation of (E)- *and* (Z)-*1,2-bis(2-naphthyl) ethylene* (**11a**) *and* (**11b**). The two phase Wittig procedure described by Tagaki *et al.*[11] was employed in the preparation of these alkenes. The *E* isomer **11a** is insoluble in benzene, the organic phase, and hence may be removed by filtration after phase separation. Recrystallization from benzene afforded 4.3 g (56%) of the alkene **11a**: m.p. 256° (lit[32] 258–259°). The benzene soluble Z isomer **11b** was recovered from the filtrate and crystallized from EtOH to give 2.1 g (28%), m.p. 105° (lit[32] 105.5–106.5°).

Preparation of the oxiranes **1–4**. The 1,2-diarylalkenes (12.5 mmol) and *m*-chloroperbenzoic acid (3.5 g, 20.3 mmol) were dissolved or suspended in 150–600 ml CH_2Cl_2. The mixture was stirred at room temp overnight, and the excess peracid then destroyed by addition of sodium thiosulfate (5%). The organic phase was then separated and washed sequentially with $NaHCO_3$ aq, water, sat NaCl aq and dried over Na_2SO_4. The volatile solvent was then removed and the residue recrystallized from appropriate solvents displayed along with the m.ps and spectral data in Table 5.

Direct irradiations of oxiranes **1**, **2** *and* **3** *in the presence of electron deficient dipolarophiles.* In a typical case, a 100 mg sample of the oxirane and 10 equivts of the dipolarophile were dissolved in 10 ml of either benzene or acetonitrile contained in a quartz or uranyl glass tube (9 cm). The transmission of the latter vessel was essentially nil below 320 nm (Table 2, p. 5). The solns were degassed and irradiated in a Rayonet source equipped with a 254 or broad band 350 nm source selected on the basis of the absorption characteristics of the oxirane employed. The excess alkenes were removed by vacuum distillation subsequent to

Table 5.

Compound No.	M.P. °C	Recrystallization Solvent	NMR (CDCl$_3$) δ
3a	215	C_6H_6	7.3-8.0 (m,14H), 4.14 (s,2H)
3b	1125	2-propanol	6.9-7.6 (m,14H), 4.3 (s,2H)
2a	163-4	CH_3OH/C_6H_6	7.22-7.95 (m,14H), 1.27 (s,6H)
2b	99-100	Aq. CH_3OH	7.05-7.65 (m,14H), 1.85 (s,6H)

irradiation. The isomers were ultimately separated by using benzene as an eluent.

Direct irradiations of the oxiranes 3 *in the presence of* (E)-*and* (Z)-2-*butene in benzene*. A suspension of **3a** or soln of **3b** (100 mg, 0.34 mmol) in 5 ml benzene was sealed with a serum cap in a pyrex test tube. The system was purged with N_2 in each case for 15 min, then cooled in an ice bath, and an equal volume of (*E*)- or (*Z*)-2-butene was condensed in the vessel. The resulting soln was allowed to warm to room temp and irradiated with broad band lamps (λ_{max} 350 nm) for a period of 3 days. The excess butene and solvent were removed under vacuum and the residual adducts and precursors separated by using benzene as an eluent. Only two adducts (**21f** and **22f**) were obtained from each oxirane (Table 2, p. 5). The ratios of **21f** to **22f** (72:28) correspond closely, regardless of the stereochemistry of the oxirane precursor (**3a** or **3b**).

Electron transfer sensitized cycloadditions of 1 *and* 4 *to electron deficient dipolarophiles*. Essentially the same procedures described for the direct irradiations of oxiranes in the presence of electron deficient dipolarophiles were employed with the exception that 40 mg (0.22 mmol) of 1,4-dicyanonaphthalene (DCN) was added as an electron transfer agent (Table 4, p. 7).

Preparation of (z)-2,3-*bis*(2-*naphthyl*)-2-*butene* (**10b**). The preparation of **10b** was carried out in accordance with the general procedure described by McMurry.[10a] The separated product was recrystallized from MeOH–hexane; 1.4 g (26%) of **10b** (mp 99°); NMR ($CDCl_3$) 6.9–7.8 (m, 14H), 2.28 (5, 6H); mass spectrum *m/e* 308.

Preparation of (E)-2,3-*bis*(2-*naphthyl*)-2-*butene* (11). A 300 mg (0.97 mmol) sample of the *Z* isomer **10b** was dissolved in 1 ml of benzene in a quartz test tube sealed with a serum cap. The soln was degassed and irradiated (λ_{max} 350 nm) for 12 hr. Removal of solvent and recrystallization of the residue from MeOH-benzene provided 280 mg of the *E* alkene; m.p. 143–4°, NMR ($CDCl_3$) 7.2–7.9 (m, 14H), 2.0 (s, 6H); mass spectrum *m/e* 308.

Triplet-triplet energy sensitized cycloadditions of 3 *to dimethyl fumarate in benzene*. A procedure similar to that used for the foregoing electron transfer sensitized cycloadditions was employed except that 40 equivs of acetophenone (or benzophenone) was used as a sensitizer in place of the electron transfer agent DCN. Furthermore, a filter system composed of uranyl glass and a saturated solution of naphthalene in ether was utilized to ensure that direct excitation of the oxiranes was avoided. That this filter system was effective was evidenced by the fact that in the absence of the sensitizer, no cycloaddition was observed. A soln of **3b** or suspension of **3a** and dimethyl fumarate was irradiated at 350 nm for 30 min. The solvents were removed *in vacuo*, and the residue was analyzed by NMR (200 MHz) to determine the relative ratio of the adducts.

Thermolysis of 3 *and* 4 *in the presence of dimethyl fumarate and maleate*. Typically, a sample of oxirane (100 mg, 0.34 mmol) was mixed with 20 equivs of the alkene and 0.5 ml acetonitrile or benzene and sealed in a thick-walled pyrex tube. The tube was then heated in a fused salt bath composed of $NaNO_2$ and KNO_3 (8.5:10 parts by weight, respectively) at 175° (for **3a** and **3b**) or 205° (for **4a** and **4b**). The solvents and alkenes were removed under reduced pressure and the relative amounts of the cycloadducts were determined by NMR (90 MHz) (Table 3, p. 6). The mixture was then separated into the individual components by tlc on silicagel plate using benzene as the eluent, which were subsequently characterized.

Acknowledgments—The authors are indebted to the National Science Foundation (Grant CHE78-00615) for providing financial support of this work. Appreciation is also expressed to Ms. Tanya Mancuso for her assistance in the preparation of this manuscript.

REFERENCES

[1] Taken in part from the dissertation submitted by John P. K. Wong in partial fulfillment for the Ph.D. requirements of the University of New Orleans, New Orleans, LA 70122 (1980).
[2] R.B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*. Verlag Chemie, Weinheim, Germany (1970).
[3a] R. S. Becker, R. O. Bost, J. Kolc, N. R. Bertoniere, R. L. Smith and G. W. Griffin, *J. Am. Chem. Soc.* **92**, 1302 (1970); [b] G. W. Griffin and A. Padwa, *Photochemistry of Heterocyclic Compounds*, (Edited by I. Buchardt), Chap. 2, pp. 41–42. Wiley, New York (1976).
[4a] A. Padwa, *Organic Photochemistry I* (Edited by O. L. Chapman); pp. 91–126, Marcel Dekker, New York (1967)[b] N. R. Bertoniere and G. W. Griffin, *Organic Photochemistry III* (Edited by O. L. Chapman), Chap. 2, pp. 115–195 (Marcel Dekker, New York (1973).
[5a] N. R. Bertoniere and G. W. Griffin *Carbenes I*, (Edited by M. Jones, Jr. and R. A. Moss) Chap. 3, pp. 305–349, Wiley, New York (1973). [b] G. W. Friffin, *Angew Chem.* **83**, 604 (1971); *ibid.* Int. Ed. Engl., **10**, 537 (1971).
[6a] G. A. Lee, *J. Org. Chem.* 41, 2656 (1976); [b] *Ibid.* 43, 4256 (1978).
[7] R. Huisgen and V. Markowski, *Tetrahedron Letters* 4643 (1976).
[8] P. Hallet, J. Muzart and J. P. Pete, *Ibid.* 2727 (1979).
[9a] S. Arakawa, *J. Org. Chem.* 42, 3800 (1977); [b] H. Kato, H. Tezuka, K. Yamaguchi, K. Nowada and Y. Nakamura, *J. Chem. Soc. Perkin I*, 1029 (1978); [c] K. Maruyama and A. Osuka, *Chem. Letters* 77 (1979).
[10a] J. E. McMurry, *Acc. Chem. Res.* 7, 281 (1974); [b] J. E. McMurry and M. P. Fleming, *J. Org. Chem.* 41 896 (1976).
[11a] W. Tagaki, I. Inoue, Y. Yano and T. Okonogi, *Tetrahedron Letters* 2587 (1974); [b] J. P. Geerts and R. H. Martin, *Bull. Soc. Chem. Belges* **69**, 563 (1960); *Chem. Abstr.* 55, 14410d (1961).
[12] A. C. Cope, P. A. Trumbull and E. R. Trumbull, *J. Am. Chem. Soc.* **80**, 2844 (1958).
[13] K. N. Houk, N. G. Rondan, C. Santiago, C. J. Gallo, R. Gandour and G. W. Griffin, **102**, 1504 (1980).
[14a] R. Huisgen, *Angew. Chem.*, Int. Ed. Engl., **2**, 633 (1963); [b] R. Huisgen, *J. Org. Chem.* 33, 2291 (1968).
[15a] E. G. Ullman and W. A. Henderson, *J. Am. Chem. Soc.* **86**, 5050 (1964); [b] D. R. Arnold and L. A. Karnischky, *ibid.* **92**, 1404
[16a] R. Huisgen, *Abstr. 24th Natl. Organic Chemistry Symposium of the American Chemical Society* No. 87; Colorado State University, Ft. Collins, Colorado, June 22–26 (1975) [b] R. Huisgen, W. Scheer and H. Huber, *J. Am. Chem. Soc.* **89**, 1753 (1967).
[17] G. W. Griffin and A. M. Trozzolo, unpublished results.
[18] T. Do-Minh, A. Trozzolo and G. W. Griffin, *Ibid*, **92**, 1402 (1970).
[19a] The rates of addition of oxiranes **2a** and **2b** to dipolarophiles is relatively slow, and irradiation times are being extended (10–20 days) in an attempt to obtain adducts; [b] N. J. Turro, *Modern Molecular Photochemistry* p. 121; Benjamin/Cummings, Menlo Part, California (1978) [c] *Ibid.* 189.

[20] R. Huisgen, *Angew. Chem.* Int. Ed. Engl. 16, 572 (1977).

[21] K. N. Houk, Chap. 4 *Pericyclic Reactions II*, pp. 181–271 and Refs. cited, Academic Press, New York (1977).

[22] K. Nishiyama, K. Ishikawa, I. Sarkar, D. C. Lankin and G. W. Griffin, *Heterocycles* 6 1337 (1977).

[23] Personal communication from Prof. K. Houk to Prof. Griffin.

[24] I. J. Lev, K. Ishikawa, N. S. Bhacca and G. W. Griffin, *J. Org. Chem.* 41, 2654 (1976).

[25] A. Albini and D. R. Arnold, *Can. J. Chem.* 56, 2985 (1978).

[26] A. Robert, J. J. Pommeret, E. Marchand A. Foucaud, *Tetrahedron* 29, 463 (1973).

[27] R. A. Grieger and C. A. Eckert, *J. Am. Chem. Soc.* 92, 7149 (1970).

[28a] M. Kayser and P. Morand, *Tetrahedron Letters* 695 (1979); [b] E. Garbisch and D. Patterson, *J. Am. Chem. Soc.* 85, 3228 (1963).

[29a] J. Berson, Z. Hamlet and W. A. Mueller, *ibid.* 84, 277 (1962); [b] R. Steinmetz, W. Hartmann and G. Schenck, *Chem. Ber.* 98, 3854 (1965).

[30] The higher percentage of non-stereospecific adducts produced from 21 and dimethyl maleate in benzene relative to acetonitrile is attributed to the higher viscosity of the former solvent and concomitant decreased efficiency of dipole photoisomerization. See A. A. Lamola and N. J. Turro, *Energy Transfer and Organic Photochemistry*. Interscience, New York (1963).

[31a] A. Dahmen, J. Hamberger, R. Huisgen and V. Markowski, *J. Chem. Soc Chem. Commun.* 1192 (1971); [b] L. M. Jackman and S. Sternhell, *Applications of Neclear Magnetic Resonance Spectroscopy in Organic Chemistry* (2nd Edn) p. 234 Pergamon Press, New York (1969).

[32] J. L. Everett and G. Kon, *J. Chem. Soc.* 1601 (1948).