tions of the molecule and the different geometry of the excited states of the β-naphthospiropyran compared to the dimethylbenzochromene as shown by the difference in their absorption spectra, particularly the 0, 0 band of the first transition (part I).[3] In this case, analysis of the second chromene transition of the spiropyran is more difficult for several reasons. Primarily, the intensity of the second transition is extremely low, compared to that of the first and the structure is virtually unresolved. Second, mixing between the first indoline transition and the second chromene transition occurs.

Becker, *et al.*,[2] have shown that competition between photochemistry and internal conversion occurs at each level of a particular vibration and further that the ratio $k_{\mathrm{IC}}/k_{\mathrm{PC}}$ can be determined for a particular sequence by consideration of the equation $\log \phi_{\mathrm{F}}(n) = \{\log[k_{\mathrm{IC}}/(k_{\mathrm{IC}} + k_{\mathrm{PC}})]\}n$ where $\phi_{\mathrm{F}}(n)$ is the relative quantum yield of fluorescence, n = vibrational quantum number of a given sequence of a particular vibrational transition, k_{PC} = rate constant for photochemistry, k_{IC} = rate constant for internal conversion, and $n = 0, 1, 2, 3\ldots$. Thus, $\log [k_{\mathrm{IC}}/(k_{\mathrm{IC}} + k_{\mathrm{PC}})]$ is the slope of a plot of $\log \phi_{\mathrm{F}}$ *vs.* n, which should be a straight line. From the $\log [k_{\mathrm{IC}}/(k_{\mathrm{IC}} + k_{\mathrm{PC}})]$ term, $k_{\mathrm{IC}}/(k_{\mathrm{IC}} + k_{\mathrm{PC}})$ and $k_{\mathrm{IC}}/k_{\mathrm{PC}}$ can be determined. Unfortunately, in the case of the spiropyrans considered here, only the absorption of β-napthospiropyran is sufficiently structured to allow determination of this ratio. Further, only one vibrational sequence of both the first and second chromene transitions can be followed clearly, the 1290- and 1370-cm^{-1} vibrations, respectively. The ratio of $k_{\mathrm{IC}}/k_{\mathrm{PC}} \simeq 2.1 \pm 0.5$ for the 1290-cm^{-1} vibration indicates that photochemistry is very competitive with internal conversion in this vibrational sequence. Further, if this were the C–O–C asymmetric stretching frequency which has approximately this value in a conjugated system, the high rate of photochemistry would be explained nicely since the primary photochemical step involves cleavage of the C–O bond.[2] The ratio $k_{\mathrm{IC}}/k_{\mathrm{PC}} \simeq 8.0 \pm 1.5$ for the 1370-cm^{-1} vibration indicates that photochemistry is much less competitive with internal conversion in this vibrational sequence of the second chromene transition. Thus, the results on β-naphthospiropyran are in agreement with and support the results obtained by Becker, *et al.*,[2] on the chromenes.

Summary

It is clear that the emission transitions of the benzospiropyrans considered are localized on the chromene half of the molecule with the exception of the 5,6′-dinitro derivative in which the emission apparently originates from the indoline portion. Further, the nature of the emissions appears to be valid as assigned. Intramolecular energy transfer between the indoline and chromene portions of the molecule clearly occurs. The relative quantum yields of emission, particularly for the β-naphthospiropyran, show and support a vibronic effect (in excited singlet states) in photochemistry.

Acknowledgment. We wish to acknowledge the assistance of Dr. Josef Michl in the performance of the experimental work and interpretation of the results for the 5,6′-dinitrobenzospiropyran.

Spectroscopy and Photochemistry of Aryloxiranes[1a]

Ralph S. Becker,[1b] Robert O. Bost, Jaroslav Kolc, Noelie R. Bertoniere, Robert L. Smith, and Gary W. Griffin[1c]

Contribution from the Chemistry Department of the University of Houston, Houston, Texas 77004, and the Chemistry Department, Louisiana State University in New Orleans, New Orleans, Louisiana 70122. *Received October 11, 1969*

Abstract: The absorption spectra of several phenyl-substituted oxiranes in 3-methylpentane at −196° are highly structured and characterized by a 0–0 band at 271 ± 3 nm with a more intense, structureless band at ~230 nm. The fluorescence emission of these compounds occurs at 285–340 nm, with a maximum at 305–310 nm. The isomeric 2,3-bis-α-naphthyloxiranes and tetraphenylepisulfide have also been studied. Irradiation into the 0–0 or higher energy absorption bands causes formation of a colored intermediate. Subsequently, the parent alkene and arylcarbene(s), and carbonyl compound(s) are formed in a manner dependent on oxirane symmetry. Phenyloxirane behaves atypically and no divalent carbon fragments are formed. A consistent mechanistic pathway is proposed to explain the photochemistry and spectroscopy of the oxiranes and their photoproducts.

Several aspects of the spectroscopy and photochemistry of phenyloxiranes have been studied.[2] Griffin and coworkers[3] have found that arylcarbenes are generated in addition to aldehydes and/or ketones upon

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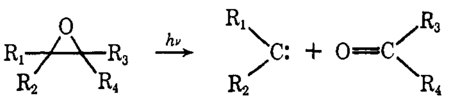
(1) (a) Taken from the thesis submitted by R. O. B. in partial fulfillment of the Ph.D. requirements, University of Houston, Houston, Texas; (b) all spectroscopy and low-temperature photochemistry were conducted at the Department of Chemistry, University of Houston, Houston, Texas 77004; (c) all compounds were synthesized and their gross ambient-temperature photochemistry studied in the Department of Chemistry, Louisiana State University in New Orleans, New Orleans, Louisiana 70122. These irradiations were conducted in quartz vessels in a Rayonet chamber reactor (The Southern New England Ultraviolet Co., Middletown, Conn.) equipped with sixteen 8-W low-pressure mercury lamps.

(2) For a preliminary report on this work see: R. S. Becker, J. Kolc, R. O. Bost, H. Dietrich, P. Petrellis, and G. W. Griffin, *J. Amer. Chem. Soc.*, 90, 3292 (1968).

(3) (a) H. Kristinsson and G. W. Griffin, *Angew. Chem. Intern. Ed. Engl.*, 4, 868 (1965); (b) H. Kristinsson and G. W. Griffin, *J. Amer. Chem. Soc.*, 88, 1579 (1966); (c) H. Dietrich, G. W. Griffin, and R. C. Petterson, *Tetrahedron Lett.*, 153 (1968); (d) P. Petrellis and G. W. Griffin, unpublished results.

photolysis of a variety of phenyloxiranes in solution at ambient or higher temperatures (eq 1). These divalent



(1)

carbon species were shown to have properties which are qualitatively and quantitatively similar to carbenes generated from diazo compounds in their reactions with alkanes,[3c] alkenes and alcohols.[3b] The presence of substituents in addition to phenyl such as cyano,[4] methyl,[5] and methoxy[6] on the oxirane ring does not adversely affect the photofragmentation, at least in those cases studied.

Trozzolo, Griffin, and coworkers,[7] using epr and optical spectroscopy, confirmed that diphenylmethylene is produced upon photolysis of both tetra- and triphenyloxirane; however, for reasons at the time unclear, neither phenylcarbene nor the expected carbonyl fragment, benzophenone, could be detected upon irradiation of triphenyloxirane despite chemical evidence to the contrary for their formation.[3b]

At this time we wish to report the results of our investigations on the ultraviolet spectroscopy and photochemistry of phenyloxirane (**1a**), *trans*- and *cis*-2,3-diphenyloxirane (**1b** and **1c**, respectively), triphenyloxirane (**1d**), tetraphenyloxirane (**1e**), tetraphenylepisulfide (**1f**), *trans*- and *cis*-2,3-bis-α-naphthyloxirane (**1g** and **1h**, respectively), *trans*-2,3-diphenyl-2,3-dimethyloxirane (**1i**), and 1,2-diphenyl-1,2-epoxycyclohexane (**2**).

1 2

a, $R_1 = C_6H_5$; $R_2 = R_3 = R_4 = H$; $X = O$
b, $R_1 = R_4 = C_6H_5$; $R_2 = R_3 = H$; $X = O$
c, $R_1 = R_3 = C_6H_5$; $R_2 = R_4 = H$; $X = O$
d, $R_1 = R_2 = R_3 = C_6H_5$; $R_4 = H$; $X = O$
e, $R_1 = R_2 = R_3 = R_4 = C_6H_5$; $X = O$
f, $R_1 = R_2 = R_3 = R_4 = C_6H_5$; $X = S$
g, $R_1 = R_4 =$ α-naphthyl; $R_2 = R_3 = H$; $X = O$
h, $R_1 = R_3 =$ α-naphthyl; $R_2 = R_4 = H$; $X = O$
i, $R_1 = R_4 = C_6H_5$; $R_2 = R_3 = Me$; $X = O$

The principal results of this investigation of aryl-substituted oxiranes include: (1) the observation of colored intermediates created in a primary photochemical process; (2) confirmation that two separate one-photon processes are involved in the fragmentation reactions, the first causing formation of a colored intermediate and the second causing photochemistry of this intermediate; (3) the characterization of hitherto uncharacterized photoproducts; (4) optical spectroscopic identification of phenylmethylene and diphenylmethylene, and (5) an interpretation of the photochemistry and thermochemistry of the products obtained in the photofragmentation process.

Results and Discussion

A. Phenyloxiranes. At low temperature (−196°) all of the phenyl-substituted oxiranes studied exhibit a highly resolved ultraviolet absorption pattern with a 0–0 band at 271 ± 3 nm and a more intense, unresolved band at approximately 230 nm (Figure 1 and Figure 2). It is interesting that the relative intensities of the vibrational bands in the low-temperature absorption spectra vary as a function of the phenyl substitution. In *trans*-2,3-diphenyloxirane (**1b**) and triphenyloxirane (**1d**) the first and third vibrational bands are more intense than in the second and fourth. Conversely in the other phenyloxiranes the second and fourth vibrational bands are dominant. Extinction coefficients for selected oxiranes are shown in Table I. Excitation into the 0–0 or higher energy absorption band causes each of these oxiranes to emit a fluorescence which is broad and poorly structured from 280 to 340 nm, with a maximum at 305–310 nm (Figure 3). Tetraphenyloxirane (**1e**) also has a broad unresolved phosphorescence emission with an onset at 360 nm (27,777 cm^{-1} or 79.5 kcal/mol) and a maximum at 404 nm. Detailed analyses of phosphorescent emissions were not carried out for the remaining phenyloxiranes considered herein; however,

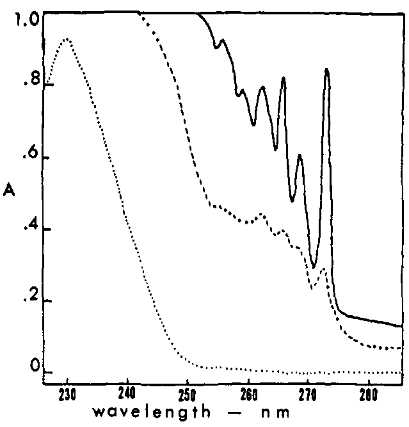


Figure 1. Absorption spectra of *trans*-2,3-diphenyloxirane: −196° (——); room temperature (– – –); lower concentration of **1b** to show transition at 230 nm (····).

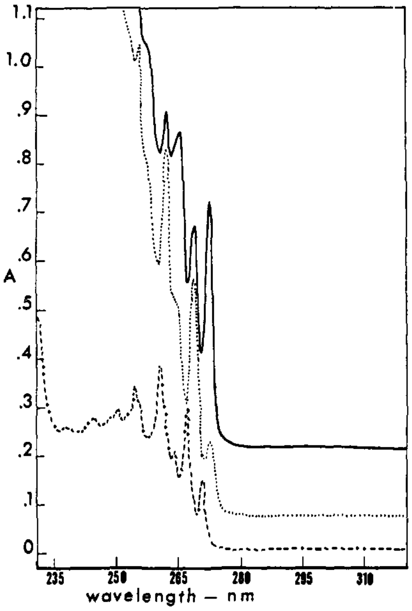


Figure 2. Absorption spectra of phenyloxirane (– – –), tetraphenyloxirane (····), and triphenyloxirane (——).

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(4) P. Petrellis, H. Dietrich, E. Meyer, and G. W. Griffin, *J. Amer. Chem. Soc.*, 89, 1967 (1967).

(5) H. Kristinsson, *Tetrahedron Lett.*, 2343 (1966).

(6) P. Petrellis and G. W. Griffin, *Chem. Commun.*, 691 (1967).

(7) A. M. Trozzolo, W. A. Yager, G. W. Griffin, H. Kristinsson, and I. Sarkar, *J. Amer. Chem. Soc.*, 89, 3357 (1967).

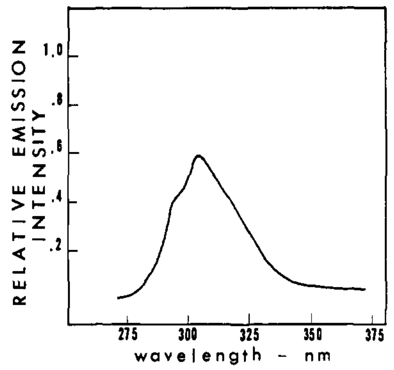


Figure 3. Emission spectrum of *cis*-2,3-diphenyloxirane at −196°.

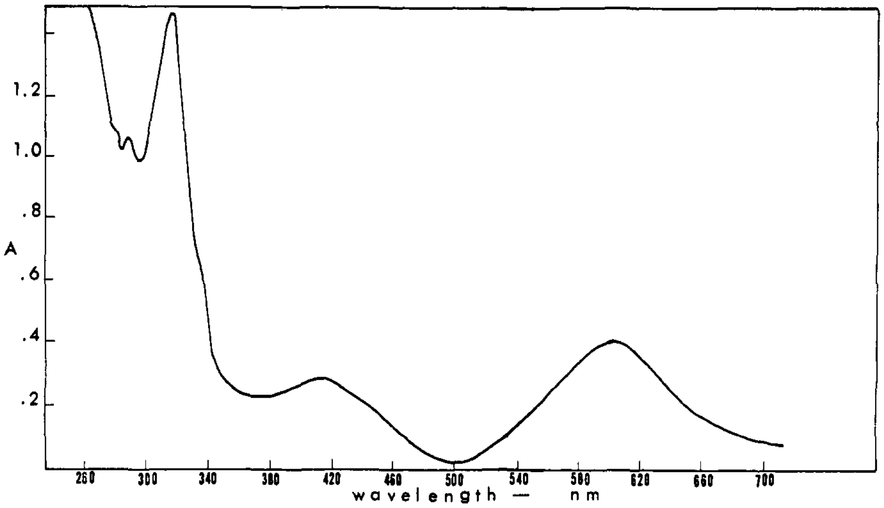


Figure 4. Absorption spectrum of the blue intermediate obtained by irradiating tetraphenyloxirane at −196° for 10 min.

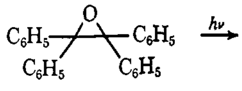
the close similarity of the absorption and fluorescence spectra of **1e** with those of the others suggests that the triplet energies will not deviate greatly from that found for **1e**. The fluorescence excitation spectrum of each compound, which reproduces the absorption spectrum, provides assurance that the emissions are intrinsic to the oxiranes.

Table I. Extinction Coefficients of Selected Oxiranes

Oxirane	Wavelength (nm)	ε
trans-2,3-Diphenyloxirane	272	510
	265	742
	261	845
	255	840
cis-2,3-Diphenyloxirane	272 (shoulder)	
	266	306
	261	415
	255	352
Tetraphenyloxirane	268	990
	262	1,510
trans-2,3-Bis-α-naphthyl-oxirane	314	1,284
	297	13,360
	286	13,040
cis-2,3-Bis-α-naphthyl-oxirane	313.5	1,020
	295	10,710
	283.5	15,055
	273.5 (shoulder)	12,780

Continuous irradiation at −196° into the 0–0 or higher energy band of all of the phenyloxiranes with the exception of phenyloxirane (**1a**) produces a colored species, with broad structureless visible absorption bands. The orange-red species obtained from *trans*- and *cis*-2,3-diphenyloxirane (**1b** and **1c**, respectively) exhibit one band with maxima at 501 nm (*trans*) and 506.5 nm (*cis*); triphenyloxirane (**1d**) yields a pink intermediate having maxima at 547 and 398 nm, while the blue intermediate from tetraphenyloxirane (**1e**) exhibits three bands (Figure 4), one at 605 nm, the second having two poorly resolved maxima at approximately 435 and 415 nm, and the third at 320 nm. The photoproduced red-purple species obtained from *trans*-2,3-diphenyl-2,3-dimethyloxirane (**1i**) and 1,2-diphenyl-1,2-epoxycyclohexane (**2**) have broad bands from 610 nm to 450 nm and maximizing at ~527 and 535 nm, respectively. In all cases the colored intermediates are stable at −196°. However, they can be bleached either by warming the sample above −180° or by irradiation into one of the visible absorption bands (*vide infra*).

Benzophenone, tetraphenylethylene, and diphenylmethylene (**3**) are obtained upon irradiation into the 0–0 or higher energy absorption band of tetraphenyloxirane (**1e**) in a rigid glass at −196° (eq 2). The tetraphenylethylene was not observed as a product in earlier studies



1e

$$(C_6H_5)_2C\!: + (C_6H_5)_2CO + (C_6H_5)_2CC(C_6H_5)_2 \quad (2)$$

3

conducted under a variety of conditions at room temperature.[3] Convincing evidence that tetraphenylethylene is a primary product and not a product of dimerization of diphenylmethylene will be presented later in connection with the discussion on *trans*-2,3-diphenyloxirane (**1b**). The emission spectrum of benzophenone consists of four sharply resolved peaks separated by deep valleys (Figure 5). A broad unresolved emission band maximizing at ~430 nm (Figure 5) is observed for tetraphenylethylene. The emission from the mixture

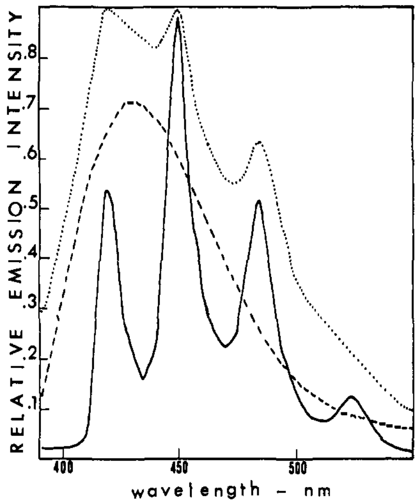


Figure 5. Emission spectra of benzophenone (——); tetraphenylethylene (- - -); product mixture of irradiated sample of tetraphenyloxirane (· · · ·).

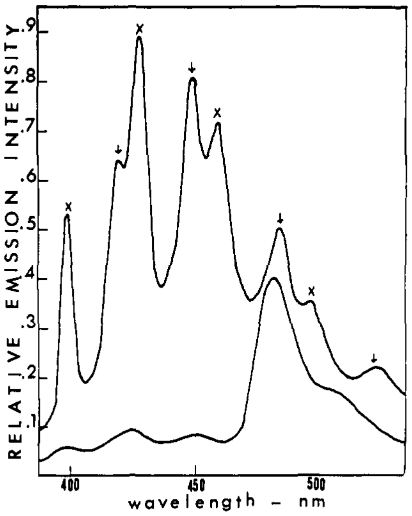
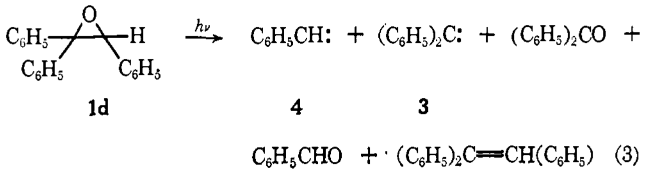


Figure 6. Upper curve shows emission spectrum of irradiated sample of triphenyloxirane (× marks the bands of benzaldehyde, → marks the bands of benzophenone); lower curve shows emission spectrum of irradiated triphenyloxirane at a different exciting wavelength to show emission of diphenylmethylene.

of photoproducts obtained from the oxirane **1e** (Figure 5) clearly shows that the valley between the first and second benzophenone peaks has been raised considerably as expected if tetraphenylethylene were present. The emission of diphenylmethylene (Figure 6) is broad and unresolved with an onset at 460 nm (21,740 cm^{-1}, 62.25 kcal/mol) and a maximum at 485 nm. This emission from the carbene and carbonyl photoproducts of **1e** was observed and identified earlier by Trozzolo, Griffin, and coworkers.[7] When an irradiated sample of **1e** is allowed to warm to room temperature and then is recooled to −196°, the emission due to diphenylmethylene (**3**) disappears and the intensity of the emission due to tetraphenylethylene, as would be expected, increases.

The mixture of photoproducts obtained from triphenyloxirane (**1d**) is more complex. Irradiation of **1d** at −196° gives benzaldehyde, benzophenone, phenylmethylene (**4**), and diphenylmethylene (**3**) as photoproducts (eq 3). All of these photoproducts are



$$\text{1d} \xrightarrow{h\nu} \underset{\mathbf{4}}{C_6H_5CH\colon} + \underset{\mathbf{3}}{(C_6H_5)_2C\colon} + (C_6H_5)_2CO + C_6H_5CHO + (C_6H_5)_2C{=}CH(C_6H_5) \quad (3)$$

generated at 40° and previously had been identified chemically and, with the exception of **4**, characterized spectroscopically in a rigid matrix.[3,7] Although there is a clear indication that triphenylethylene also is formed, the data are not as well defined as in the corresponding case of tetraphenyloxirane (**1e**). The emission spectrum of an irradiated sample of triphenyloxirane (**1d**) is shown in Figure 6. *trans*-Stilbene is not a primary photoproduct from the photolysis of triphenyloxirane since the characteristic *trans*-stilbene emission bands at 335, 350, and 370 nm[8] are absent. Our emission spectral data on an authentic sample of *trans*-stilbene are in agreement with that previously reported.[8] The emission of diphenylmethylene (**3**) at 485 nm is observable, but no emission due to phenylmethylene (**4**) is detected. The relative ratios of the products produced upon irradiation of triphenyloxirane (**1d**) may account for our failure to observe emission from **4**. From the products shown in eq 3 it is apparent that fragmentation of triphenyloxirane occurs in two ways: (a) to give benzophenone and phenylmethylene, and (*b*) to give benzaldehyde and diphenylmethylene. Comparison of the peak intensities in the spectrum of the product mixture (Figure 6) with those of a solution containing equimolar amounts of benzophenone and benzaldehyde indicates that the preferred mode of fragmentation is to benzaldehyde and diphenylmethylene (~70%).[9] It also is clear from the relative amounts of benzhydryl- and benzylmethyl ethers formed (85% and 15%, respectively) when methanol was used as a trapping agent and the reaction is run at 40°, that the fragmentation occurs preferentially to give diphenylmethylene and benzaldehyde.[3d] Since phenylmethylene is formed in lower yield in the fragmentation of **1d** and its emission (*vide infra*) overlaps the short-wavelength edge of the emission due to benzaldehyde, it is possible that the former could escape detection. That phenylmethylene is produced upon photolysis of **1d**, however, is apparent from the fact that the emission of *trans*-stilbene appears after the irradiated sample of triphenyloxirane (**1d**) has been warmed and recooled. Dimerization of phenylmethylene is the only reasonable mechanism for formation of *trans*-stilbene under the conditions described. In a similar fashion dimerization of diphenylmethylene produces tetraphenylethylene (*vide supra*).

Irradiation of either *trans*- or *cis*-2,3-diphenyloxirane (**1b** or **1c**, respectively) yields benzaldehyde, phenylmethylene, and the corresponding *trans*- or *cis*-stilbene. All but the last compound previously had been characterized chemically among the photoproducts of **1b** and **1c** obtained in a variety of solvents at 40°.[3b] Two studies show that this stilbene is a primary photoproduct of **1b** and does not arise from dimerization of phenyl-

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[8] S. Malkin and E. Fischer, *J. Phys. Chem.*, **68**, 1153 (1964).

[9] Although it is recognized peak heights are not an exact measure of concentration ratios, it is believed that, since in this case all variables except concentration have been kept constant, this method provides a reasonable method of estimating the product ratios.

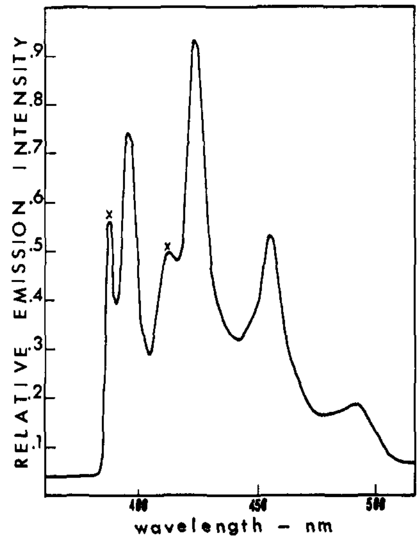

Figure 7. Emission spectrum of irradiated *cis*-2,3-diphenyloxirane, showing emission of phenylmethylene (marked with ×) and benzaldehyde.

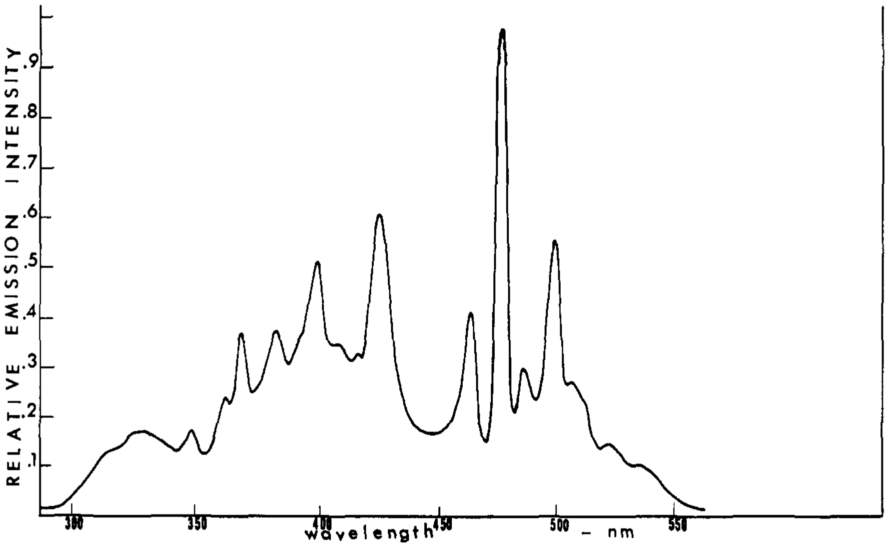

Figure 8. Emission spectrum of an irradiated sample of phenyloxirane.

methylene. As discussed earlier, *trans*-stilbene is not observed when the sample of triphenyloxirane (**1e**) is irradiated, but is formed only after the sample has been warmed sufficiently to become fluid. This suggests that the 3-methylpentane glass (at −196°) is sufficiently rigid that bimolecular reactions do not occur. In a subsequent study a glass much "harder" than 3-methylpentane, namely isononane–isooctane (1:1), was employed. The viscosity of this glass is approximately 5 × 10^5 greater than that of 3-methylpentane.[10] Dimerization of the divalent carbon fragments certainly would not occur in such a rigid matrix, and yet, *trans*-stilbene is still formed upon irradiation of *trans*-2,3-diphenyloxirane in this matrix. Thus we conclude that the *trans*-stilbene formed must arise *via* a unimolecular process. Furthermore it was demonstrated in a similar way that the tetraphenylethylene mentioned above which arises from **1e** is also formed by an intramolecular process and not by dimerization of diphenylmethylene.

The emission of phenylmethylene is observed at 389 and 414 nm, on the edge of the benzaldehyde emission peaks (Figure 7). An excitation spectrum is very difficult to obtain in this case because the emission of phenylmethylene is obscured by the onset of the benzaldehyde emission. However, verification that the assigned emission belongs to phenylmethylene was accomplished by warming the glass and recooling the solution. The bands at 389 and 414 nm then disappear and the emission intensity of *trans*-stilbene increases in the case of *trans*-2,3-diphenyloxirane (**1b**) or appears for the first time in the case of *cis*-2,3-diphenyloxirane (**1c**). *trans*-Stilbene has been shown (*vide supra*) to be a product of dimerization of phenylmethylene.

Although the absorption and fluorescence emission spectra of phenyloxirane (**1a**) are consistent with the spectra of the other phenyl-substituted oxiranes, the photochemistry of phenyloxirane is atypical both in rigid matrices at −196° and at 40° in solution.[8b] Unlike the other oxiranes irradiation into the 0–0 band at −196° does not produce an *observable* colored intermediate. The emission spectrum of an irradiated sample is shown in Figure 8. The fluorescence from the oxirane **1a** is a broad, poorly structured emission extending from 285 to 340 nm. The mixture of photoproducts includes benzyl radical, phenylacetaldehyde, and a small amount of styrene. The benzyl radical was identified by its absorption,[11] emission,[11,12] and excitation spectra. In Figure 8, the sharply resolved emission from 460 nm extending to longer wavelengths arises from benzyl radical. The formation of styrene, an expected photoproduct, is postulated on the basis of a shift in the maximum wavelength of the broad oxirane emission from 310 to 330 nm. The small amount of styrene formed is not sufficient to allow observation of the expected vibrational structure of the emission.

The formation of rearrangement products analogous to phenylacetaldehyde is a process not seen in the other

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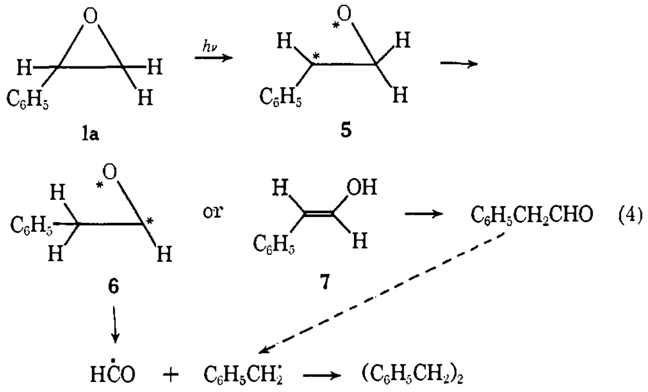
(10) H. Greenspan and E. Fischer, *J. Phys. Chem.*, **69**, 2466 (1965).

(11) P. M. Johnson and A. C. Albrecht, *J. Chem. Phys.*, **48**, 851 (1968).

(12) G. Porter and E. Strachan, *Spectrochim. Acta*, **12**, 299 (1958).

phenyl-substituted oxiranes studied. The emission system at 399, 425, and 457 nm is due to phenylacetaldehyde. There is still some question regarding the assignment of the emission system at 348, 362, 368, and 372 nm; however, the emission spectrum of 1,2-diphenylethane exhibits this same pattern although the only pathway to 1,2-diphenylethane in this system is benzyl radical dimerization. Results discussed earlier have shown that bimolecular reactions do not occur in the rigid media employed in this study. While thin layer chromatography indicates that the authentic sample of phenylacetaldehyde used is homogeneous, there is still some question regarding its purity. The emission spectroscopic studies as carried out in this study are generally more sensitive than other methods of establishing purity. Thus, no unequivocal assignment can be made at this time for the emission originating at 348 nm. We also find that prolonged irradiation of phenylacetaldehyde under conditions simulating those employed with **1a** at −196° produces benzyl radical which could also account for the appearance of this species. A mechanism for the photoreactions of **1a** consistent with the products obtained is shown in eq 4. It is proposed that irradiation of **1a** causes formation of an initial intermediate such as **5**. In a second step, a 1,2-hydrogen migration to carbon or oxygen may occur to produce **6** or **7** (eq 4). The former may fragment directly or give phenylacetaldehyde which in turn decarbonylates to the observed benzyl radical. We believe that the primary source of benzyl radical at −196° is photofragmentation of **6**. This conclusion is based upon the fact that benzyl radical appears 6–10 times faster from the styrene oxide than from phenylacetaldehyde.



Independent liquid phase studies of the photochemistry of phenyloxirane (**1a**) as well as 2,2-diphenyloxirane, which behaves similarly, have been made by Elam, *et al.*[13] The preliminary results of this study, conducted in benzene (40°), indicate that the aldehydes are more photolabile than the oxiranes at 2537 Å. The reason(s) for the apparent contrasting behavior observed for **1a** in rigid and fluid media is of interest and presently under investigation. Phenylacetaldehyde was identified as a photoproduct from **1a** although the major product under these conditions is bibenzyl which undoubtedly arises by coupling of benzyl radicals.[14] Carbon-14 labeling studies, to be reported in detail later, exclude any rearrangement involving initial homolysis of the C_β–O oxirane bond in **1a** to give **8** followed by 1,2-phenyl migration to give phenylacetaldehyde directly (eq 5). While such a homolysis may appear energetically unfavorable it seemed conceivable that the energy required to sever this bond might be less than anticipated as a result of synchronous formation of the new bond to the aromatic nucleus, *i.e.*, that the energy requirements are diminished by aryl participation. Finally, all attempts to detect phenylmethylene and/or methylene itself, both of which could conceivably be formed from **1a** by photofragmentation, proved unsuccessful at 40°.

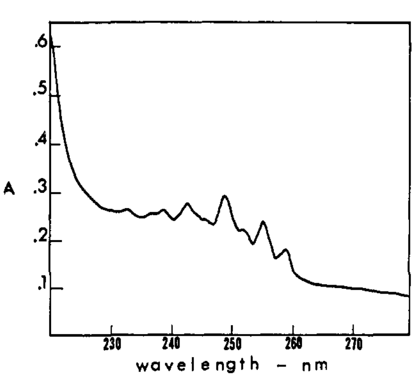
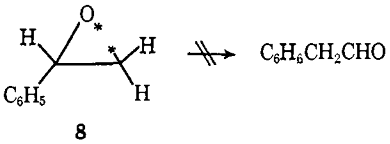


Figure 9. Absorption spectrum of 1,2-diphenyl-1,2-epoxycyclohexane.



(5)

The absorption spectrum of *cis*-1,2-diphenyl-1,2-epoxycyclohexane (**2**) is shown in Figure 9. It is seen that the relative absorption intensities resemble those found for phenyloxirane (**1a**) (Figure 2) and *cis*-2,3-diphenyloxirane (**1c**). *trans*-2,3-Diphenyl-2,3-dimethyloxirane (**1i**)[5] exhibits the same general absorption pattern and relative intensities. It is noteworthy that the first and third vibrational bands in the spectrum of *trans*-2,3-diphenyloxirane (**1b**) are more intense than the second and fourth bands, whereas in the case of *trans*-2,3-diphenyl-2,3-dimethyloxirane (**1i**) the second and fourth bands are stronger than the first and third.

Irradiation of *trans*-2,3-diphenyl-2,3-dimethyloxirane (**1i**)[5] at −196° yields acetophenone, as determined by comparing the emission observed from an irradiated sample with the known phosphorescence of acetophenone.[15a] An alkene is also produced which is probably *trans*-1,2-diphenyl-1,2-dimethylethylene, on the basis of previous results. The emission spectrum of an irradiated sample of 1,2-diphenyl-1,2-epoxycyclohexane (**2**) was composed of a phosphorescence similar to that of acetophenone and an emission similar to that of *cis*-stilbene. These emissions show that two of the same

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(13) M. Elam, P. Petrellis, H. Kristinsson, and G. W. Griffin, unpublished results. The rates of the photochemical reactions of the 2-phenyl- and 2,2-diphenyloxiranes were compared with the corresponding aldehydes by monitoring the rate of appearance of bibenzyl and diphenylmethane, respectively, using gas chromatography with benzylylcyclohexane as an internal standard. No spectroscopic corrections were applied since **1a** and phenylacetaldehyde have similar absorption characteristics at 2537 Å.

(14) Padwa and coworkers independently observed that 30–40% yields of bibenzyl are obtained upon irradiation of phenylacetaldehyde; A. Padwa, D. Crumrine, R. Hartman, and R. Layton, *J. Amer. Chem. Soc.*, **89**, 4435 (1967).

(15) (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1967, p 286; (b) p 506.

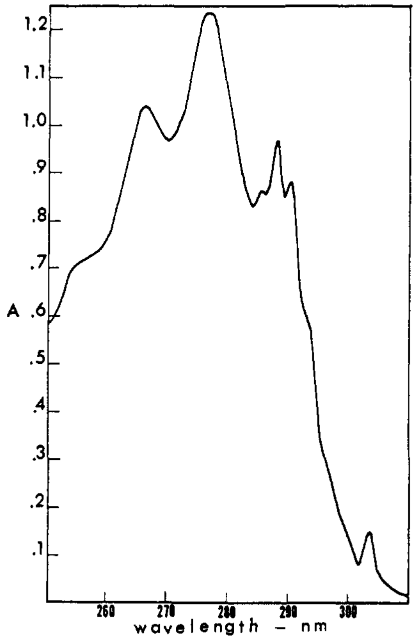


Figure 10. Absorption spectrum of *cis*-2,3-bis-α-naphthyloxirane.

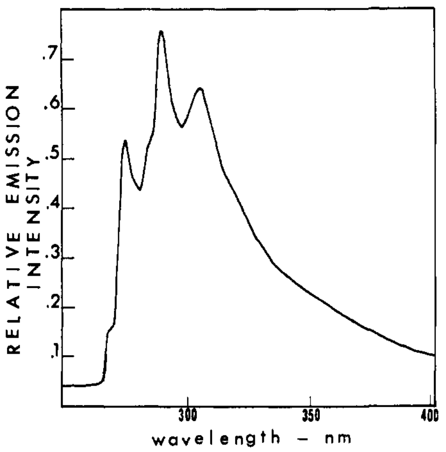
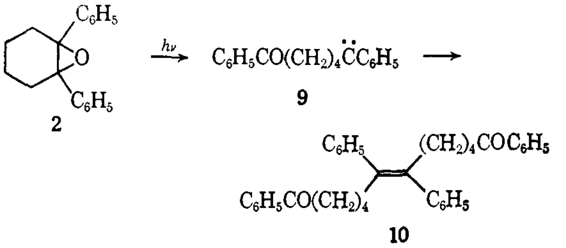


Figure 11. Fluorescence emission of *cis*-2,3-bis-α-naphthyloxirane.

photochemical processes observed with **1i** also occur with **2**, *i.e.*, extrusion of an oxygen atom from the oxirane ring to give an alkene and fragmentation of one carbon–oxygen bond and the carbon–carbon bond of the oxirane ring to form a ketone and arylcarbene. In the case of the cyclic oxirane **2**, however, the fragmentation leads to the ketocarbene **9** rather than to independent fragments. The phosphorescence, similar to that of acetophenone, which is observed from the photoproducts of **2** probably arises from **9** since the tetramethylene chain separating the keto group from the methylene site would not be expected to affect the emission properties of the aroyl moiety. No emission which could be ascribed to the arylcarbene moiety is observed. It is not unlikely that this emission is obscured by the aroyl and alkene emissions. Evidence for the presence of **9** among the photoproducts was obtained by allowing an irradiated sample of **2** to warm to room temperature. Upon recooling the sample an emission quite similar to that of *trans*-stilbene appears. This observation could be rationalized by assuming that in the fluid state dimerization of the keto carbene **9** can occur to give **10** (eq 6).[16]



(6)

B. Tetraphenylepisulfide (1f) and 2,3-Bis-α-naphthyloxiranes (1g and 1h). The low-temperature absorption spectrum of tetraphenylepisulfide (**1f**) consists of two sharp peaks at 265 and 257 nm and a shorter wavelength band of such intensity that no maximum is apparent. Irradiation of tetraphenylepisulfide produces a green intermediate which absorbs in a broad band with a maximum at approximately 650 nm and a second band in the region 400–425 nm. Continued irradiation produces tetraphenylethylene, as identified by its broad emission with a maximum at 401 nm (Figure 5). No emission which could be assigned to thiobenzophenone was observed. Similar results were obtained at 40° and no thiobenzophenone or diphenylcarbene could be detected upon irradiation of **1f** in benzene. Under these conditions tetraphenylethylene is the major product although some 9,10-diphenylphenanthrene is also formed.[17]

The low-temperature absorption spectrum of *trans*-2,3-bis-α-naphthyloxirane (**1g**) consists of a highly resolved pattern with a 0–0 band at 312 nm and additional bands at 302, 300, 298, 287, and 276 nm. In addition, an intense band appears in the spectrum at shorter wavelength for which no maximum was determined. The low-temperature absorption spectrum of *cis*-2,3-bis-α-naphthyloxirane (**1h**) is similar to that of the *trans* isomer **1g** and consists of a highly resolved pattern with a 0–0 band at 313 nm and additional bands at 300, 298, 295, 287, 276, and 265 nm (Figure 10). An intense band at shorter wavelength for which no maximum was determined is also apparent in the spectrum. The fluorescence emission spectra of *trans*-2,3-bis-α-naphthyloxirane (**1g**) and *cis*-2,3-bis-α-naphthyloxirane (**1h**) are essentially identical and consist of a resolved group of three peaks at 325, 340, and 355 nm (Figure 11). The fluorescence excitation spectrum of each isomer coincides with the observed absorption spectrum.

Upon irradiation of either *trans*- or *cis*-bis-α-naphthyloxiranes (**1g** and **1h**) a purple color develops. The colored intermediate from the *trans*-naphthyloxirane **1g** has a strong, broad, structureless absorption spectrum with a maximum at 575 nm and shoulders at 485 and 455 nm. The purple colored species generated upon irradiation of the *cis* and *trans* isomers have absorption spectra in the region 680–450 nm with maxima at 570 nm and 575 nm, respectively. As shown in Table I, the extinction coefficients of the *cis* and *trans* isomers

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(16) The photochemistry of the corresponding 1,2-diphenyl-1,2-epoxycyclopentane as well as the monophenyl epoxycyclopentane and cyclohexane has also been studied (40°) and will be reported at a later date; I. Sarkar and G. W. Griffin, unpublished results.

(17) G. W. Griffin, O. P. Strausz, A. M. Trozzolo, and R. C. Petterson, unpublished results; see T. Sato, Y. Gato, T. Tohyama, S. Hayashi, and K. Hata, *Bull. Chem. Soc. Jap.*, 40, 2975 (1967), for a study of the photochemistry of *trans*-2,3-diphenylepisulfide.

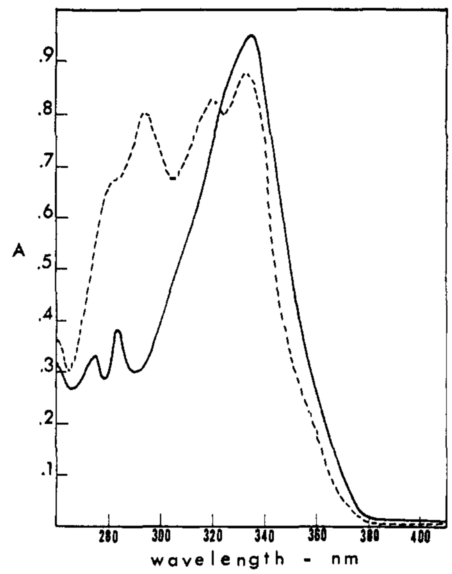


Figure 12. Absorption spectra of *cis*- (- - -) and *trans*-1,2-bis-α-naphthylethylene (——).

1h and **1g** are approximately equal. Of interest is the observation that irradiation of a solution containing **1h**, the *cis* isomer, produces a color which is only 10% as intense as that obtained from the *trans* isomer **1g** when equal concentrations are used. It may be concluded that the colored intermediate must be formed ten times faster from the *trans* isomer than from the *cis* isomer. Alternatively, the photostationary state in the *cis* case could be more highly displaced toward the oxirane.

cis- and *trans*-1,2-bis-α-naphthylethylene are intrinsically interesting alkenes from the spectroscopic standpoint. The absorption spectra of the two isomers differ from each other (Figure 12). On the other hand, the fluorescence emissions for the two isomers are virtually identical (Figure 13) with onsets at 358 ± 2 nm and maxima at 402 ± 1 nm. This is in striking contrast to the emission properties of the corresponding stilbenes. As mentioned earlier, *trans*-stilbene exhibits a finely structured emission at 335, 350, and 370 nm, whereas the emission of *cis*-stilbene is broad and unresolved, with a maximum at 421 nm.

Irradiation of *trans*-2,3-bis-α-naphthyloxirane (**1g**) produces *trans*-1,2-bis-α-naphthylethylene and α-naphthaldehyde, as revealed by emission studies, although the phosphorescence emission of α-naphthaldehyde is obscured to a great extent by the long-wavelength tail of the fluorescence due to the alkene. This result might have been anticipated in view of the relative emission quantum yields of the two photoproducts. The fluorescence quantum yield of the alkene is expected to be high, whereas the phosphorescence quantum yield of α-naphthaldehyde is known to be 0.03 ± 0.01.[18] Thus, extensive fragmentation of **1g** to the aldehyde would be required in order for α-naphthaldehyde to be observed in the presence of the alkene.

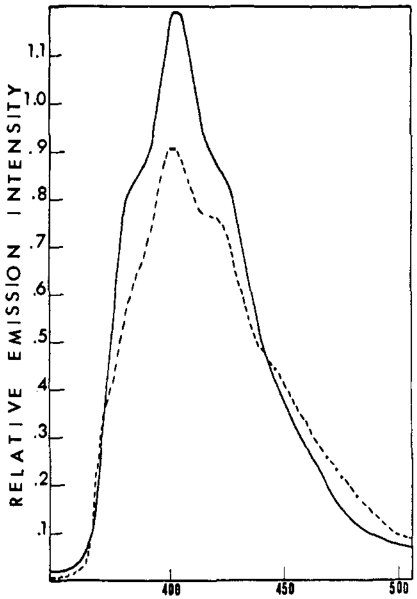
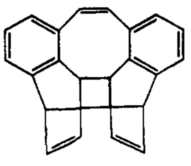
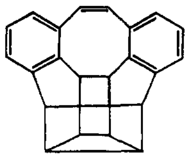


Figure 13. Emission spectra of *cis*- (- - -) and *trans*-1,2-bis-α-naphthylethylene (——).

When a sample of *cis*-2,3-bis-α-naphthyloxirane (**1h**) is irradiated two products are detected by emission spectroscopy. One product was shown to be α-naphthaldehyde by comparison of its phosphorescence with that of an authentic sample of α-naphthaldehyde. A second emission with bands at 325, 340, 358, 375, and 395 nm is also observable. Emission attributable to *cis*-1,2-bis-α-naphthylethylene is conspicuously absent and should be detected if it were generated. The observed emission is consistent with the presence of a stilbene chromophore in the molecule.[15b] A photocyclization and oxidation of the stilbene–dihydrophenanthrene–phenanthrene type to give, ultimately, picene is ruled out based on the fact that the spectroscopic properties of picene do not match those observed for the photolysis product mixture. Both hydrocarbons **11a** and **11b** have structures consistent with the observed results and could arise by intramolecular bridging of the 5 and 8 positions on the *cis*-1,2-bis-α-naphthylethylene or the corresponding positions on the oxirane followed by deoxygenation of the resulting product. The latter seems more likely in view of the proximity of the reactive centers. We tend to favor hydrocarbon **11a** as the compound responsible for the emission band system originating at 325 nm. This is primarily based on the fact that the band system appears immediately. The bands are observable during the first emission spectral scan. Photobridging of **11a** to give **11b** depends upon the presence of **11a** and requires additional photosteps. Therefore, we do not believe it likely that **11b** would appear as rapidly as the hydrocarbon observed.



11a



11b

Conclusions

In two of the systems studied [*i.e.*, tetraphenyloxirane (**1e**) and *trans*-2,3-bis-α-naphthyloxirane (**1g**)] two discrete one-photon processes are observed. The first process involves formation of the colored intermediate.

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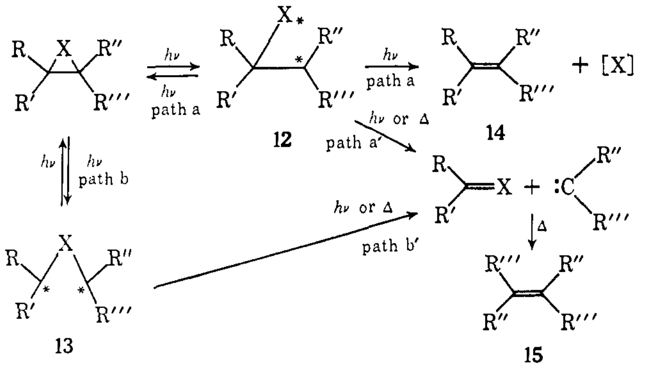
(18) V. Ermoloev and A. Terenin, *Soviet Phys. Usp. Engl. Transl.*, 3, 423 (1960).

In the second step recyclization to the oxirane or fragmentation to a carbene and ketone (or aldehyde) may occur *from this intermediate.* That the colored intermediate is implicated in the fragmentation processes was established by irradiating solely into the visible absorption bands of the intermediate and noting that bleaching occurs with simultaneous production of the original oxirane and final photoproducts. On the basis of these results, it is assumed that the initial step in the photofragmentation of the oxiranes as well as the episulfide **1f** is the same and the mechanism delineated below is consistent with the experimental results obtained.



The comparative photochemistry of **1b** and **1d** as well as the matrix viscosity study (*vide supra*) demonstrate that alkenes are formed from oxiranes by an intramolecular heteroatom extrusion process as that outlined in path a. Photolysis of triphenyloxirane does not produce *trans*-stilbene or tetraphenylethylene as primary photoproducts whereas *trans*-stilbene is formed from *trans*-2,3-diphenyloxirane (**1b**). While the absence of crossover products from **1d** excludes an intermolecular path for alkene formation it is possible that the intermediate **12** is not the colored precursor which ultimately fragments to give a carbene *via* path a′. Conceivably C–C bond scission *via* path b occurs to give **13** in a competitive reaction and this is followed by fragmentation to a carbene (path b′). It is possible to explain all products and recyclizations on the basis of intermediate **12**. Although it is possible that **13** is produced,[19] **13** *cannot be the exclusive intermediate,* because **13** could not lead to the alkene **14**.

As mentioned earlier *trans*-stilbene has not been characterized among the photoproducts of **1b** at room temperature. This result is explicable on the basis of competing reactions. At high (ambient) temperatures, the reaction rate *via* path a′ (or formation of **13**) may be so fast that it completely dominates the photochemistry of *trans*-2,3-diphenyloxirane (**1b**). However, as the temperature is lowered, the rates of reaction by paths a and a′ (or rates of formation of **12** and **13**) become comparable, and the products of both reactions are observed.

Experimental Section

General. Solutions used in the spectroscopic studies were 10^{-3}–10^{-4} *M* and 3-methylpentane was used as a solvent unless otherwise specified. This solvent was distilled from sodium and, prior to use, passed through a neutral silica gel column.

All absorption spectra were recorded on a Cary Model 15 spectrophotometer. The sample was contained in a rectangular cell with a path length of 2 mm and flat optical quartz or Suprasil windows. The cell was immersed in liquid nitrogen contained in a dewar with flat optical quartz or Suprasil windows.

The emission apparatus consisted of a 1-kW Xenon exciting lamp, a Bausch and Lomb grating monochromator, an Aminco grating analyzing monochromator, and an EMI 9558B photomultiplier tube. Emission and excitation spectra were recorded from the front face of the cell. No corrections to the emission spectra have been made for varying efficiency of the analyzing system as a function of wavelength.

All melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. The nmr spectra were recorded on a Varian A-60 nmr spectrometer, with 1% tetramethylsilane as an internal standard. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Materials. Phenyloxirane (**1a**) was obtained from styrene by essentially the same procedure described by Cope.[20] The oxiranes *trans*-2,3-diphenyloxirane (**1b**), *cis*-2,3-diphenyloxirane (**1c**), triphenyloxirane (**1d**), and tetraphenyloxirane (**1e**), as well as the tetraphenylepisulfide (**1f**) were prepared according to published procedures with minor modifications.[20,21]

Preparation of *cis*- and *trans*-2,3-Bis-α-naphthyloxiranes (1h and 1g). A mixture of the *cis* and *trans* isomeric oxiranes was synthesized according to the procedure described by Mark.[22] Separation was effected by liquid–liquid partition chromatography.[23] Recrystallization from 2-propanol yielded the pure *cis* [mp 167.5–168.5°; nmr ($CDCl_3$) δ 4.98 (s, 2, oxirane), ~7.4 (m, 14, naphthyl)], and the pure *trans* [mp 142–144°; nmr ($CDCl_3$) δ 4.33 (s, 2 oxirane), ~7.6 (m, 14, naphthyl)] oxiranes (**1h** and **1g**, respectively).

Preparation of *cis*- and *trans*-1,2-Bis-α-naphthylethylenes. A mixture of the *cis* and *trans* isomers was prepared by the Wittig procedure.[24] To a solution of 13.1 g (0.05 mol) of triphenylphosphine in 200 ml of xylene was added 8.8 g (0.05 mol) of α-(chloromethyl)-naphthalene (Columbia Organic Chemicals Co., Inc., Columbia, S. C.) in 100 ml of xylene. The mixture was heated under reflux for 24 hr and the α-naphthyltriphenylphosphonium chloride (16 g; 73%) which deposited was collected on a filter after this solution had cooled.

To a solution containing 17.5 g (0.04 mol) of α-naphthyltriphenylphosphonium chloride and 6.24 g (0.04 mol) of α-naphthaldehyde (Aldrich Chemical Co., Milwaukee, Wis.) in 200 ml of absolute ethanol was added 8.6 g (0.16 mol) of sodium ethoxide in 100 ml of ethanol. The resulting mixture was poured into water and the isomeric alkenes were extracted with benzene. The organic phase was washed three times with water and dried over anhydrous sodium sulfate. The volatile solvent was removed under vacuum and the isomeric bis-α-naphthylethylenes were separated by fractional crystallization from ethanol. Subsequent recrystallization gave the pure *cis* [mp 105–107° (lit.[24] 103.4°)] and the pure *trans* [mp 161–163° (lit.[25] 164–165°)] alkenes.

Preparation of *trans*-2,3-Diphenyl-2,3-dimethyloxirane (1i). To the Grignard reagent prepared from 60.5 g (2.5 g-atoms) of magnesium and 206 ml (2.1 mol) of bromobenzene was added 207 g (1.4 mol) of 3-phenyl-2-butanone.[26] The reaction mixture was then poured into a cold solution of 10% hydrochloric acid and the 2,3-diphenyl-2-butanol extracted with chloroform. The organic phase was then washed three times with water, dried over anhydrous sodium sulfate, and the volatile solvent removed under vacuum.

To a solution of 225 g (1.0 mol) of the crude 2,3-diphenyl-2-butanol in approximately 600 ml of toluene was added 1.0 g of iodine. The resulting mixture was heated under reflux for 22 hr. Recrystallization from methanol after standard isolation procedures afforded 98 g (0.47 mol) of the pure *trans*-2,3-diphenyl-2-butene, mp 104° (lit.[27] 105).

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[26] Sharp and Dohme, Inc., British Patent No. 684,124 (1952); *Chem. Abstr.*, **48**, 1438*c* (1954).

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With minor variations the procedure of Cope was employed for the oxidation of this *trans*-2,3-diphenyl-2-butene.[20] To a solution of 46.5 g (0.22 mol) of *trans*-2,3-diphenyl-2-butene in 200 ml of chloroform which had been cooled to 20° was added 45 ml of a 40% peracetic acid solution containing 4 g of sodium acetate. The temperature was maintained below 35° during the course of the addition. The resulting reaction mixture was then stirred for 22 hr at room temperature after which it was poured into cold water. The oxirane was extracted with methylene chloride and the organic phase stirred with a 10% sodium carbonate solution, washed with water until neutral, dried, and the solvent removed. Recrystallization from methanol yielded *trans*-2,3-diphenyl-2,3-dimethyloxirane (60%), mp 107° (lit.[28] 107°).

Preparation of 1,2-Diphenyl-1,2-epoxycyclohexane (2). The procedure described by Cope[20] for the preparation of stilbene oxide was employed in this case. A solution containing 0.24 g (1.0 mmol) of 1,2-diphenylcyclohexene, prepared according to published procedures,[29,30] in 4.0 ml of methylene chloride was cooled to 10° and 1 ml of a 40% solution of peracetic acid containing 0.05 g of sodium acetate was added at such a rate that the temperature did not rise above 40°. The mixture was stirred at room temperature for 24 hr and then poured into water. The oxirane was extracted with methylene chloride, and the organic phase washed with a dilute sodium carbonate solution prior to being dried over anhydrous sodium sulfate. The solvent was then removed and the residue (0.2 g) was recrystallized from methanol to give the pure oxirane **2**, mp 77–78°.

Anal. Calcd for $C_{18}H_{18}O$: C, 86.30; H, 7.25. Found: C, 86.57; H, 7.36.

Acknowledgment. All low-temperature spectroscopy and photochemistry were supported by a grant from the Robert A. Welch Foundation, held by R. S. B. The preparative and ambient temperature photochemical studies reported herein were supported by grants from the Petroleum Research Fund (PRF-2813-A1), administered by the American Chemical Society, the Army Research Office (Durham) (ARO-D-31-124G174), and the National Institutes of Health (DHEW-1-RO1-GM14667).

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Photodifluoramination of Alkanes and Alkenes

Carl L. Bumgardner, Ernest L. Lawton,[1] Kenneth G. McDaniel, and Halbert Carmichael

Contribution from the Department of Chemistry,
North Carolina State University, Raleigh, North Carolina 27607.

Received July 10, 1969

Abstract: Selectivity ratios for photodifluoramination of *n*-butane, *n*-butyl fluoride, ethyl chloride, and ethyldifluoramine were determined by analyzing the isomeric mixture of alkyldifluoramines produced by irradiation of N_2F_4 with these substrates. Kinetic and stoichiometric information about the photodifluoramination process was obtained from a study of the photolysis of N_2F_4 with methane. Irradiation of N_2F_4 with propylene and isobutylene results not only in substitution of NF_2 for H but addition of F and NF_2 to the double bond. The F was found mainly on the terminal carbon atom. The experimental data are rationalized by reaction schemes which have as a common step photolysis of NF_2 into atomic fluorine and fluoronitrene, NF.

The observation[2] that NF_2 radicals (available from the equilibrium $N_2F_4 = 2NF_2$) absorb in the region of 2600 Å suggested that this system should show some interesting photochemistry. Exploratory experiments[3] in which N_2F_4 was irradiated at 2537 Å with alkanes indicated that the major process was substitution of a hydrogen atom by an NF_2 group, photodifluoramination, reminiscent of photochlorination. Similar treatment of alkenes and alkynes resulted in addition of the elements of NF_3 to the multiple bond.[3–5] Formation of these and analogous products from other substrates[6,7] was rationalized by postulating that NF_2 underwent photolysis to give fluoronitrene, NF, and atomic fluorine.

To test this hypothesis we have now (a) ascertained selectivity patterns for the substitution reaction by studying the photodifluoramination of *n*-butane, 1-fluorobutane, chloroethane, and difluoraminoethane; (b) obtained kinetic and stoichiometric information by examining the photodifluoramination of methane; and (c) determined orientational preferences in the addition reaction by investigating the photodifluoramination of propylene and isobutylene.

Results

The experimental techniques employed in our selectivity study were similar to those used by Fredricks and Tedder[8] to study halogenations in the gas phase. However, photodifluoramination was carried out in a static system, whereas halogenations were conducted in a flow system. The basic assumption of radical selectivity studies is that the relative amounts of isomeric products formed from a given hydrocarbon are equal to the relative rates of hydrogen abstraction at any position in the molecule, corrected to a per-hydrogen basis. The selectivity ratios relative to the methyl

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