CO_2, forming the known *n*-butoxytrimethylsilane, whose boiling point and ir and nmr properties agreed completely with those of an authentic sample.[11]

Registry No.—**3**, 30882-86-1; **4a**, 30882-87-2; **4b**, 30882-88-3; **4c**, 30882-89-4; **4e**, 30882-90-7; **5a**, 30882-91-8; **5b**, 30882-92-9; **5c**, 30882-93-0; **5d**, 30882-94-1; **5e**, 30882-95-2; **6**, 30882-96-3.

[11] J. Fertig, W. Gerrard, and H. Herbst, *J. Chem. Soc.*, 1488 (1957).

Preparation, Characterization, and Photofragmentation of the Isomeric 1,4-Bis(2,3-diphenyloxiranyl)benzenes

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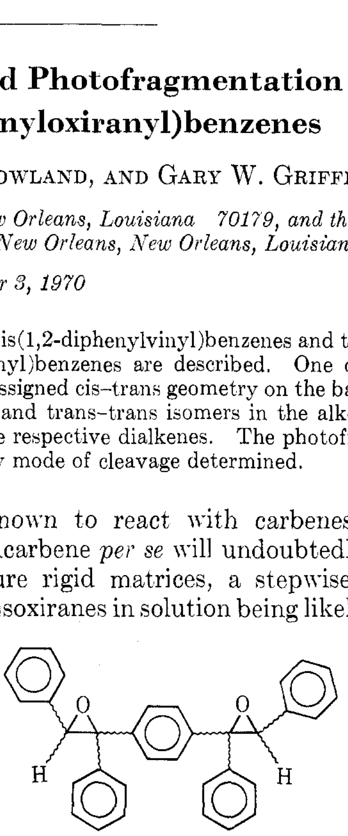
The preparation and separation of the three isomeric 1,4-bis(1,2-diphenylvinyl)benzenes and their epoxidation to give the six diastereoisomeric 1,4-bis(2,3-diphenyloxiranyl)benzenes are described. One of the dialkenes and the two bisoxiranes derived from it are unambiguously assigned cis–trans geometry on the basis of pmr data. Tentative structural assignments for the remaining cis–cis and trans–trans isomers in the alkene and oxirane series are made on the basis of the ultraviolet spectra of the respective dialkenes. The photofragmentation of the bisoxiranes in solution has been studied and the primary mode of cleavage determined.

Previous studies have demonstrated that aryl-substituted oxiranes fragment photochemically yielding aryl carbenes and carbonyl compounds.[2-6] Esr and optical spectral investigations have provided direct evidence for the formation of diphenylmethylene upon photofragmentation of tri- and tetraphenyloxirane.[7] More recently optical spectroscopic evidence for the formation of phenylmethylene upon photolysis of the isomeric 2,3-diphenyloxiranes also has been obtained.[6] In independent studies Trozzolo and coworkers have observed the esr spectra of two dicarbenes, namely *m*- and *p*-phenylenebis(phenylmethylene), upon irradiation of 1,3- and 1,4-bis(α-diazobenzyl)benzene, respectively, in rigid matrices.[8,9] The esr spectra of quintet *m*-phenylenebis(phenylmethylene) was independently reported by Itoh[10] who oriented the diazo precursor in a single crystal of benzophenone.

The observation that the unsymmetrical oxirane, triphenyloxirane, fragments preferentially (85%) to give diphenylmethylene and benzaldehyde[6] suggested that the isomeric 1,4-bis(2,3-diphenyloxiranyl)benzenes (**1**) would fragment in a similar manner and perhaps provide additional precursors for *p*-phenylenebis(phenylmethylene) (**2**), a transient of considerable theoretical as well as potential practical interest as a cross-linking agent for a broad variety of polymers having functionality known to react with carbenes. Observation of the dicarbene *per se* will undoubtedly require low temperature rigid matrices, a stepwise fragmentation of the bisoxiranes in solution being likely.



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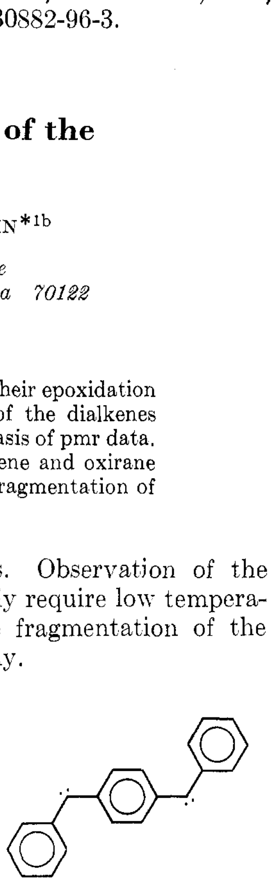

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The bisoxiranes **1** in principle may exist in six diastereoisomeric forms and we were also interested in the possibility that the mode of fragmentation might vary as a function of the stereochemistry of the precursor. Therefore we have prepared, separated, and characterized the three isomeric 1,4-bis(1,2-diphenylvinyl)benzenes and the six diastereoisomeric 1,4-bis(2,3-diphenyloxiranyl)benzenes derived from them by peracid oxidation and studied the fragmentation pattern of the latter in methanol.

Results and Discussion

1,4-Bis(1,2-diphenylvinyl)benzenes.—A mixture of the three isomeric alkenes was prepared from *p*-dibenzoylbenzene *via* a Grignard addition–dehydration sequence previously described by Buu-Hoi and coworkers.[11] These authors report the preparation of "α"-distilbenzylbenzene, mp 74°, a substance characterized only by elemental analyses. No structural assignment or mention of the other potential isomers was made. Microscopic examination revealed that amorphous materials were obtained in our attempts to repeat the earlier work and to crystallize the product from ethanol as described. Neither heating under reflux in ethanol containing a trace of iodine nor in toluene containing *p*-toluenesulfonic acid converted the mixture to a single, stable isomer. One of the isomers, mp 172–174°, eventually crystallized from *n*-heptane

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[1] (a) Taken from the dissertation submitted by N. R. B. in partial fulfillment of the Ph.D. requirements, Louisiana State University in New Orleans, New Orleans, La. (b) Author to whom inquiries regarding this communication should be directed, Louisiana State University in New Orleans. (c) One of the laboratories of the Southern Marketing and Nutrition Research Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] H. Kristinnsson and G. W. Griffin, *Angew. Chem., Int. Ed. Engl.*, **4**, 868 (1965).

[3] H. Kristinnsson and G. W. Griffin, *J. Amer. Chem. Soc.*, **88**, 1579 (1966).

[4] H. Kristinnsson, *Tetrahedron Lett.*, 2343 (1966).

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

[6] R. S. Becker, R. O. Bost, J. Kolc, N. R. Bertoniere, R. L. Smith, and G. W. Griffin, *ibid.*, **92**, 1302 (1970).

[7] A. M. Trozzolo, W. A. Yager, G. W. Griffin, H. Kristinnsson, and I. Sarkar, *ibid.*, **89**, 3357 (1967).

[8] A. M. Trozzolo, R. W. Murray, G. Smolinsky, W. A. Yager, and E. Wasserman, *ibid.*, **85**, 2526 (1963).

[9] E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo, and G. Smolinsky, *ibid.*, **89**, 5076 (1967).

[10] K. Itoh, *Chem. Phys. Lett.*, **1**, 235 (1967).

[11] N. P. Buu-Hoi, T. B. Loo, and N. D. Xuong, *J. Chem. Soc.*, 3964 (1957).

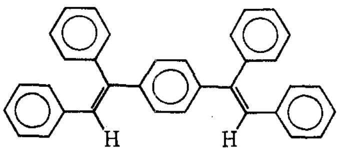
after preliminary purification of the crude reaction mixture by passage through an acidic alumina column with benzene as the eluent. The other two isomers, mp 145-146 and 109-110°, then deposited in succession in crystalline form from the solution. After the initial crystallizations subsequent batches of solid deposited as mixtures which we found necessary to separate by fractional crystallization from 2-propanol and/or diethyl ether (more an art than a science). In our experience n-heptane remains the only solvent discovered from which a freshly prepared mixture would crystallize. Repeated attempts to separate these isomers using glc, tlc, and column chromatography proved unsuccessful.

The gross structural features of the 1,4-bis(1,2-diphenylvinyl)benzenes were confirmed by the following data. (a) The mass spectra of all three isomers exhibit the expected parent peak at m/e 434 and the combustion analytical data are consistent with the proposed structures. (b) Significant absorption bands at 3050 cm^{-1} with a weak shoulder at 2900 cm^{-1} are apparent and are compatible with a phenyl-substituted ethylenic structure. (c) The pmr spectra of these dienes confirm the presence of 2 vinyl and 24 aromatic protons, although in one case (for example, the cis-trans[12] isomer **4**) one of the vinyl protons is obscured by the aromatic multiplet. The pmr data for the isomeric 1,4-bis(1,2-diphenylvinyl)benzenes are summarized in Table I. While chemical and spectroscopic data confirm the gross structural features of **3**, **4**, and **5**, no distinction between the cis-cis and trans-trans isomers **3** and **5**, respectively, could be made by pmr spectroscopy since the vinyl protons in each isomer are equivalent. The fortuitous overlap of the aromatic protons of **4** with one of the nonequivalent vinyl protons renders the assignment of structure solely by pmr tenuous even in this case. That the 1,4-bis(1,2-diphenylvinyl)benzene isomer melting at 109-110° does indeed possess the cis-trans geometry is apparent from the pmr spectra of the pair of bisoxiranes derived from **4** which also exhibit two singlet signals for the oxiranyl hydrogens (*vide infra*).

Table I

Pmr Data for the Isomeric 1,4-Bis(1,2-diphenylvinyl)benzenes

Mp of isomer, °C	Vinyl protons, τ	Aromatic protons (major peaks), τ
172-174	2.95 (2 H)	2.88, 2.67 (24 H)
109-110	?, 3.02 (1 H)	2.94, 2.90, 2.87, 2.78, 2.74, 2.68 (25 H)
145-146	2.95 (2 H)	2.96, 2.77, 2.69 (24 H)



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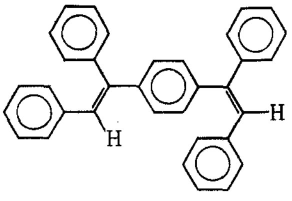

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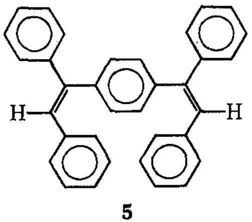
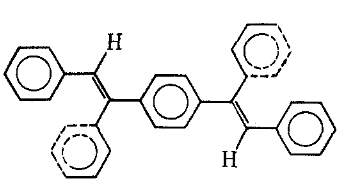


5

The ultraviolet absorption spectral data for the three isomeric 1,4-bis(1,2-diphenylvinyl)benzenes proved useful and are summarized in Chart I along with data for several related systems. The structural feature of primary significance in determining the position of the long wavelength band in the ultraviolet spectra of these systems is the extent of coplanarity which may be achieved along the linear molecular skeleton. Structural features, such as cis double bonds and branching phenyl groups, which cause deviations from planarity result in the expected hypsochromic shifts.[13] The absorption at longer wavelengths observed in the 1,4-bis(2-phenylvinyl)benzenes (p-distyrylbenzenes) relative to the 1,4-bis(1,2-diphenylvinyl)benzene system is therefore expected. *A priori* one would predict that, in either series, the isomer with the longest trans linear backbone should absorb at the longest wavelength.

A study of molecular models reveals that a completely planar conformation is not possible in the case of the three isomeric 1,4-bis(1,2-diphenylvinyl)benzenes. However, it is apparent that maximum conjugation and thus minimum steric interaction is achieved in the case of the cis-cis isomer if the 1- and 1′-phenyl substituents are rotated perpendicular to the plane of the *trans,trans*-1,4-bis(2-phenylvinyl)benzene chromophore present in conformer **6**. The corresponding conformation **7** for the trans-trans isomer is inaccessible because of the interference encountered between the ortho hydrogens of the cis coplanar phenyl groups. A more stable conformation **8** for this isomer possesses two planar trans stilbene-like structures rotated slightly with respect to the phenylene group in such a manner that the adverse steric interactions existing in **7** are reduced at the expense of coplanarity.



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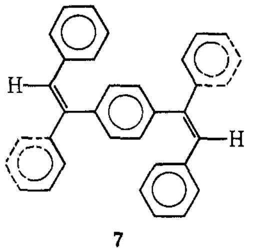

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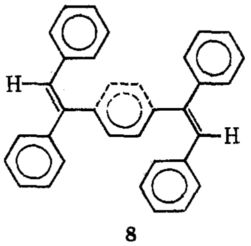

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On the basis of these considerations the following structural assignments are proposed. That isomer melting at 172-174° (λ_{max} 333 nm) is assigned structure **3** while that isomer of melting point 145-146° (λ_{max}

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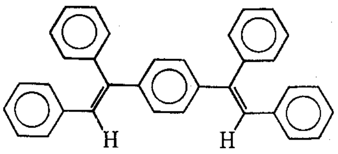
[12] This and subsequent designations of this type refer to the relationship of the monosubstituted phenyl groups to each other in the respective stilbenyl substituents.

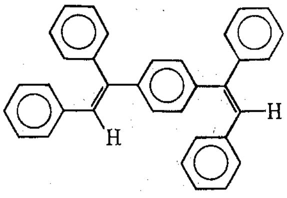
[13] R. N. Jones, *J. Amer. Chem. Soc.*, **65**, 1818 (1943).

CHART I

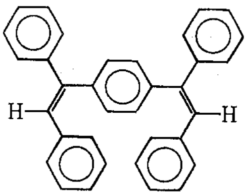
ULTRAVIOLET ABSORPTION MAXIMA OF THE ISOMERIC 1,4-BIS(1,2-DIPHENYLVINYL)BENZENES AND RELATED SYSTEMS



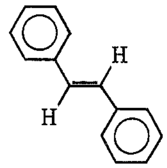
mp 172–174°: λ_{max}333 nm (ϵ 35,500) (benzene)



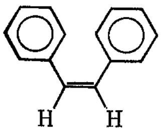
mp 109–110°; λ_{max} 330 nm (ϵ 24,000) 301 (33,000) (hexane)



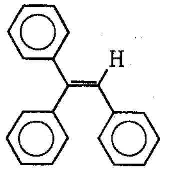
mp 145–146°; λ_{max} 295 nm (ϵ 36,000) (hexane)



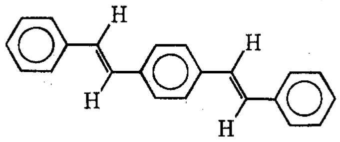
λ_{max} 295 nm (ϵ 27,000)[a]



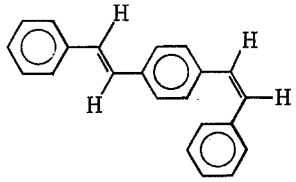
λ_{max} 280 nm (ϵ 10,450)[a]



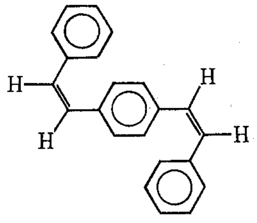
λ_{max} 299 nm (ϵ 18,200)[c]



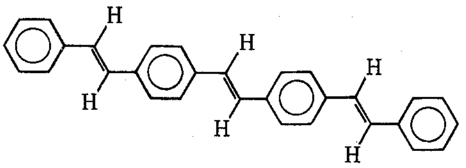
λ_{max} 350 nm (ϵ 57,000)[d]



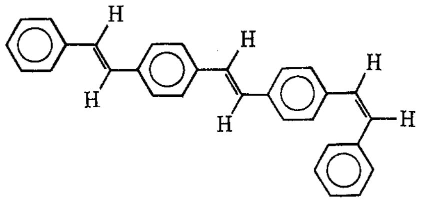
λ_{max} 331 nm (ϵ 36,500)[d]



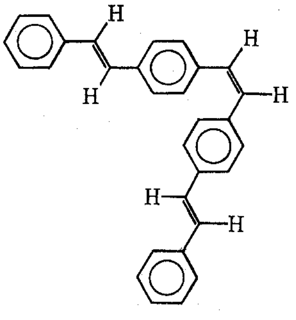
λ_{max} 314 nm (ϵ 17,700)[d]



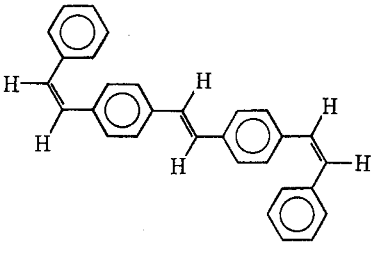
λ_{max} 384 nm (ϵ 89,300)[a]



λ_{max} 372 nm (ϵ 68,100)[a]



λ_{max} 316 nm (ϵ 52,100), 353 (41,000)[a]



λ_{max} 359 nm (ϵ 48,800)[a]

[a] S. Misumi, M. Kuwana, and M. Nakagawa, *Bull. Chem. Soc. Jap.*, **35**, 143 (1962). [b] R. N. Beal and E. M. F. Roe, *J. Chem. Soc.*, 2755 (1953). [c] H. Suzuki, *Bull. Chem. Soc. Jap.*, **33**, 389 (1960). [d] S. Misumi, M. Kuwana, K. Murashima, and M. Nakagawa, *ibid.*, **34**, 1833 (1961).

295 nm; approximately the same wavelength as triphenylethylene but with twice the molar extinction coefficient) is assigned the trans–trans structure **5**.

1,4-Bis(2,3-diphenyloxiranyl)benzenes.—The bisoxiranes (Chart II) were prepared from the three isomeric 1,4-bis(1,2-diphenylvinyl)benzenes by epoxidation with *m*-chloroperoxybenzoic acid.[14] The literature confirms that such oxidations invariably result in stereospecific cis addition to the olefin.[15] Epoxidation of the 1,4-bis(1,2-diphenylvinyl)benzenes **3**, **4**, and **5**, however, may give rise to two isomeric bisoxiranes since attack at the two vulnerable sites may occur on the same or alternate sides of the molecule. The symmetrical diolefins **3** and **5** each may give rise to a *dl* and *meso* mixture of bisoxiranes, whereas in the unsymmetrical case of **4** two *dl* pairs may in principle be formed.

As expected, a total of six bisepoxy derivatives were obtained—two from each bisalkene—and their melting points are tabulated along with the data for the precursors.

	Cis–cis	Cis–trans	Trans–trans
Alkenes	172–174° (**3**)	109–110° (**4**)	145–146° (**5**)
Oxiranes	258–260° (**9**)	189–190° (**11**)	150–152° (**13**)
	200–206° (**10**)	149–151° (**12**)	111–113° (**14**)

The separation of the oxiranes **9** and **10** obtained from the common precursor **3** was achieved by taking advantage of their relative solubilities in chloroform. The residue **9** remaining after extraction of the more soluble isomer **10** was recrystallized by dissolution in boiling chloroform and subsequently adding methanol. Final purification of **10** may be accomplished by recrystallization from 2-propanol. The mixture of **11** and **12** obtained from **4** was separated by fractional

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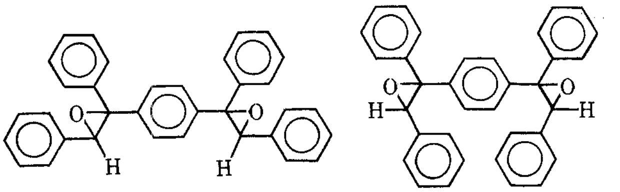
(14) N. N. Schwartz and J. H. Blumbergs, *J. Org. Chem.*, **29**, 1976 (1964).

(15) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 112.

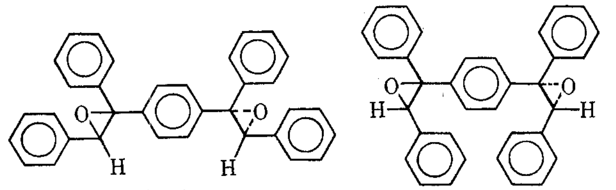
Chart II

Diastereoisomers of 1,4-Bis(2,3-diphenyloxiranyl)benzene



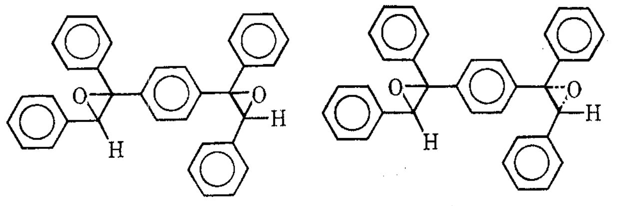
cis–cis–meso

trans–trans–meso



cis–cis–dl

trans–trans–dl



cis–trans–dl (1)

cis–trans–dl (2)

crystallization from 2-propanol. The mixture of **13** and **14** obtained upon oxidation of **5** was dissolved in boiling 2-propanol. After collection of **13** the solvent was removed and the residue dissolved in methanol from which **14** crystallized.

The wavelength of the bands in the ultraviolet spectra of the bisoxiranes vary with skeletal geometry; however, they are essentially identical for pairs derived from common precursors. The extinction coefficients of all six isomers are essentially the same at the wavelength of maximum absorption but differ markedly at 2537 Å, the accessible wavelength required to effect fragmentation (Table II).

Table II

Ultraviolet Absorption Maxima of the Diastereoisomeric 1,4-Bis(2,3-diphenyloxiranyl)benzenes

Isomer	Skeletal geometry	λ_{max}, nm	ϵ at λ_{max}, ϵ	ϵ at 253.7 nm	Solvent
9	Cis–cis[a]	241	39,500	21,600	Heptane–THF
10	Cis–cis	241	44,600	23,500	Heptane
11	Cis–trans	231	39,200	5,600	Heptane
12	Cis–trans	231	43,600	6,200	Heptane
13	Trans–trans[a]	225	42,000	2,600	Heptane
14	Trans–trans	225	43,700	2,500	Heptane

[a] Suggested by the ultraviolet spectra of the parent diolefins.

The pmr spectra of the isomeric bisoxiranes **9–14** are consistent with the proposed 1,4-bis(2,3-diphenyloxiranyl)benzene structures. Complex multiplet signals due to the aromatic protons are apparent in the pmr spectra and also are characteristic for isomer pairs derived from common precursors. In fact, the overall spectra of the bisoxiranes derived from each isomer of 1,4-bis(1,2-diphenylvinyl)benzene are strikingly similar. As indicated earlier the presence of two oxiranyl singlet signals in the spectra of **11** and **12** demonstrates that these bisoxiranes, and therefore the parent 1,4-bis(1,2-diphenylvinyl)benzene (mp 109–110°), have cis–trans geometry. The pmr spectra of **9** and **10** as well as **13** and **14** are not helpful in distinguishing between the cis–cis and trans–trans precursors **3** and **5** or between *dl* and *meso* bisoxiranes because of the symmetry and resulting magnetic equivalency of the pertinent protons. The pmr spectral data are summarized in Table III.

Table III

Pmr Data for the Six Diastereoisomers of 1,4-Bis(2,3-diphenyloxiranyl)benzene

Isomer	Oxirane protons, τ	Aromatic protons (major peaks), τ
9	5.71 (2 H)	2.91, 2.89, 2.82, 2.67 (24 H)
10	5.65 (2 H)	2.88, 2.83, 2.76, 2.60 (24 H)
11	5.74 (1 H) 5.67 (1 H)	2.90, 2.83, 2.80, 2.66 (24 H)
12	5.75 (1 H) 5.68 (1 H)	2.92, 2.83, 2.80, 2.67 (24 H)
13	5.67 (2 H)	2.91, 2.68 (24 H)
14	5.73 (2 H)	2.94, 2.71 (24 H)

The existence of polymorphic pairs appears unlikely because repeated recrystallization of the individual bisoxiranes from a variety of solvents produces no change in the melting points.[16]

Photofragmentation in Methanol.—Theoretically three fragmentation patterns are possible for the 1,4-bis(2,3-diphenyloxiranyl)benzenes as shown in eq 1. In order to determine the extent to which each of the reaction paths is followed, methanol solutions of each of the six isomeric 1,4-bis(2,3-diphenyloxiranyl)benzenes were irradiated with 2537-Å light, the carbenes being trapped as their methyl ethers.[17] Thus *p*-phenylenebis(phenylmethylene) (**2**) is trapped as 1,4-bis(α-methoxybenzyl)benzene (**17**) and 1-benzoyl-4-(phenylmethylene)benzene (**15**) as 1-benzoyl-4-(α-methoxybenzyl)benzene (**18**). The extent to which paths 1, 2, and 3 were followed was ascertained by determining the relative amounts of the high-molecular-weight fragments **17**, **18**, and **16** formed upon irradiation. Conclusions drawn from the low-molecular-weight fragments, benzyl methyl ether (from phenylcarbene) and benzaldehyde, would be ambiguous as both are formed by more than one pathway.

An irradiation period of 3 min (low conversion) was used as both 1-benzoyl-4-(α-methoxybenzyl)benzene and *p*-dibenzoylbenzene are photolabile. Their destruction, however, is only detectable if the irradiation period exceeds 5 min. *p*-Dibenzoylbenzene was not detected and experiments in which it was added to the

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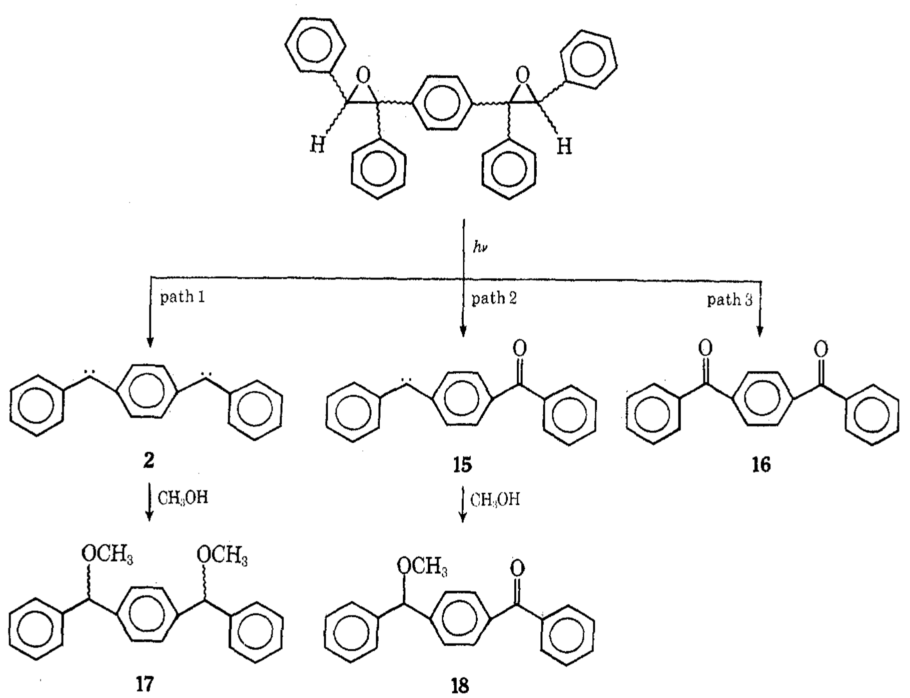
(16) A close similarity of the pmr, ir, and uv spectra of pairs of bisoxiranes from common precursors was also observed with the related 1,4-bis(3-phenyl-2-oxiranyl)benzene system. That the suspected compounds are indeed diastereoisomers was demonstrated by determining the pmr spectra of the two *trans,trans*-1,4-bis(3-phenyl-2-oxiranyl)benzenes obtained from *trans,trans-p*-distyrylbenzene in deuteriochloroform containing tris(dipivalomethanato)europium(III), the "shift reagent" reported recently [C. C. Hinkley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969)]. In both cases substantial downfield shifts in the resonance peaks are observed and the aromatic signals, which are normally broad singlets, are split into complex multiplets. Distinct oxiranyl and aromatic signals in the pmr spectrum of a mixture of the europium complexes of the two compounds demonstrate that they are not polymorphic modifications of a single isomer.

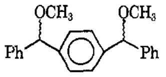
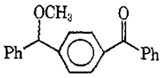
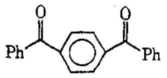
(17) W. Kirmse, L. Horner, and H. Hoffman, *Justus Liebigs Ann. Chem.*, **614**, 19 (1958).



(1)

irradiated solutions indicated that it could be detected in quantities representing only 2% of the total area. Although 1,4-bis(α-methoxybenzyl)benzene exists in two diastereoisomeric forms, their separation could not be effected *via* glc and therefore *dl*/*meso* ratios could not be determined. The results are given in Table IV.

TABLE IV
RELATIVE DIRECTIONS OF PHOTOFRAGMENTATION OF THE SIX DIASTEREOISOMERIC 1,4-BIS(2,3-DIPHENYLOXIRANYL)BENZENES IN METHANOL

Isomer			
	%	%	%
9	74	26	—
10	75	25	—
11	73	27	—
12	74	26	—
13	70	30	—
14	69	31	—

The geometry of the bisoxirane precursor had little effect on the relative direction of fragmentation.

Triphenyloxirane has been shown to fragment preferentially (85%) to give diphenylcarbene.[6] Thus, on a statistical basis one would predict probabilities for paths 1, 2, and 3 of 72, 26, and 2% assuming that the oxirane rings react independently of each other. This is very close to what is actually observed (Table IV). Thus, it seems unlikely that a dicarbene, *per se*, ever actually existed in solution but that the oxirane rings fragmented in sequence, the second not reacting until the first had been converted to the methyl ether. This does not, however, exclude the possibility that the dicarbene can exist in an unreactive rigid matrix at −196° where bimolecular reactions are excluded. The methanol trapping data indicate that it is highly probable that the dicarbene would be formed upon irradiation of the bisoxiranes in rigid matrices provided the lifetime of the initially formed carbene is sufficiently long.

Experimental Section

General.—Melting points were determined on a Thomas-Hoover capillary melting point apparatus[18] and are uncorrected. Infrared spectra were recorded on Perkin-Elmer 137 and 337 spectrophotometers. The ultraviolet absorption spectra were run on a Beckman DB spectrophotometer. The pmr spectra were taken on a Varian A-60 nmr spectrometer using $CDCl_3$ as the solvent with tetramethylsilane as an internal standard unless otherwise specified. The mass spectra were determined on a Perkin-Elmer MS 270. An F & M model dual column programmed temperature gas chromatograph equipped with a 3-ft OV-1 (3% on Chromsorb G HP) column was used for glc determinations. The instrument was operated isothermally at 220°. Silica gel G layers on glass plates were used in thin layer chromatographic separations. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Photofragmentation in Methanol.—Methanol solutions ($1-6 \times 10^{-3}$ *M*) of the six 1,4-bis(2,3-diphenyloxiranyl)benzenes were irradiated for 3 min in a Rayonet photochemical reactor (The Southern New England Ultraviolet Co., Middletown, Conn.) equipped with sixteen 2537-Å lamps. The product distribution was calculated from glc peak areas (measured on a Du Pont 310 curve resolver) which were corrected for detector response [1,4-bis(α-methoxybenzyl)benzene-1-benzoyl-4-(α-methoxybenzyl)benzene-*p*-dibenzoylbenzene, 1:0.813:0.704, w:w:w].

Preparation of the Isomeric 1,4-Bis(1,2-diphenylvinyl)benzenes (3–5).—A mixture of the three isomers was prepared in 96% yield employing the procedure described by Buu-Hoi[11] with the exception that tetrahydrofuran rather than diethyl ether was used as the solvent for *p*-dibenzoylbenzene. The resulting oily mixture was decolorized by passage through three acidic alumina columns with benzene as the solvent. Approximately 60% of the clear residue obtained after removal of the benzene under vacuum was crystallized from *n*-heptane upon standing over a 3-week period. The three individual isomers were then separated by fractional crystallization from 2-propanol. Frequently a virtually inseparable mixture, mp 122–132°, of the two higher melting isomers was obtained. It was found that separation could usually be achieved with difficulty if the recrystallizing solvent was changed to diethyl ether. The three isomers thus obtained were *cis,cis*-**3**, mp 172–174° (*Anal.* Calcd for $C_{34}H_{26}$: C, 93.97; H, 6.03. Found: C, 94.07; H, 6.09); *cis,trans*-**4**, mp 109–110° (Found: C, 93.88; H, 5.98); *trans,trans*-**5**, mp 145–146° (Found: C, 93.84; H, 6.13).

Preparation of the Isomeric 1,4-Bis(2,3-diphenyloxiranyl)benzenes (9–14).—In a typical experiment 0.43 g (1.0 mmol) of the

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[18] Use of a company or product name by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

1,4-bis(1,2-diphenylvinyl)benzene was dissolved in approximately 15 ml of chloroform and 0.45 g (2.2 mmol) of solid *m*-chloroperoxybenzoic acid (85%) (Aldrich Chemical Co., Milwaukee, Wis.) added slowly with stirring. The reaction mixture was then stirred at room temperature overnight. The progress of the reaction was followed by tlc [R_f 0.6 (diolefin), 0.42 (monoepoxides), and 0.26 (bisepoxides)] using silica gel G plates which were developed with benzene–Skelly B (1:1, v/v). Spots were located by spraying with 5% sulfuric acid in ethanol followed by charring. After the reaction was complete (~20 hr) the excess peracid was destroyed by the addition of a sodium sulfite solution, the reaction mixture washed with aqueous sodium bicarbonate (10%), the organic phase separated and dried over anhydrous sodium sulfate, and the volatile solvent removed under vacuum. The residue (0.45 g, 97%) was further purified by thick layer chromatography on 1-mm silica gel G plates. Pairs of isomers were separated by fractional crystallization as already described. The isomers thus obtained were **9**, mp 258–260° (*Anal.* Calcd for $C_{34}H_{26}O_2$: C, 87.52; H, 5.62. Found: C, 87.22; H, 5.62); **10**, mp 200–206° (Found: C, 87.21; H, 5.58); **11**, mp 189–191° (Found: C, 87.65; H, 5.58); **12**, mp 149–151° (Found: C, 87.61; H, 5.66); **13**, mp 150–152° (Found: C, 87.44; H, 5.44); **14**, mp 111–113° (Found: C, 87.26; H, 5.76).

Preparation of 1-Benzoyl-4-(α-hydroxybenzyl)benzene.—To 5 g (17.5 mmol) of *p*-dibenzoylbenzene in tetrahydrofuran was added 0.5 g of sodium borohydride (Alfa Inorganics, Beverly, Mass.). The mixture was stirred at room temperature for 4 hr after which the excess $NaBH_4$ was destroyed by the slow addition of a 5% solution of sulfuric acid. The products were extracted with chloroform, the organic phase was washed with water, dried over anhydrous sodium sulfate, and the solvent was removed under vacuum. The desired product was separated from the totally reduced 1,4-bis(α-hydroxybenzyl)benzene and the unreacted *p*-dibenzoylbenzene on 1-mm silica gel G plates which were developed with benzene–methanol (9:1, v/v) [R_f 1.0 (*p*-dibenzoylbenzene), 0.43 (1-benzoyl-4-(α-hydroxybenzyl)benzene), and 0.29 (1,4-bis(α-hydroxybenzyl)benzene)]. The residue (0.25 g, 50%) was recrystallized from benzene–hexane to give pure 1-benzoyl-4-(α-hydroxybenzyl)benzene: mp 93–95°; infrared (KBr) 1600 (C=O), 3500 cm^{-1} (OH); pmr τ ~2.2 (m, 14, aromatic), 4.0 (s, 1, methine), 6.7 (s, 1, hydroxyl).

Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.30; H, 5.60. Found: C, 83.36, H, 5.60.

Preparation of 1-Benzoyl-4-(α-methoxybenzyl)benzene (18).—The ether was prepared from 1-benzoyl-4-(α-hydroxybenzyl)benzene according to the procedure described by Gillis.[19] To 3.4 g (12 mmol) of 1-benzoyl-4-(α-hydroxybenzyl)benzene in approximately 50 ml of dimethyl sulfoxide was added 4 g of powdered sodium hydroxide and 8.5 g (60 mmol) of methyl iodide. The mixture was stirred at room temperature overnight. The reaction mixture was then poured into water, the product extracted with chloroform, the organic phase washed with water, dried over anhydrous sodium sulfate, and the solvent removed under reduced pressure. The residue (3.7 g, 100%) was further purified by passage through a neutral alumina column using benzene as the solvent. The residue after the benzene had been removed under vacuum crystallized slowly upon standing at ~5°. Recrystallization from methanol at ~5° gave pure 1-benzoyl-4-(α-methoxybenzyl)benzene: mp 46–48°; infrared 1620 cm^{-1} (C=O); pmr τ ~2.2 (m, 14, aromatic), 4.52 (s, 1, methine), 6.5 (s, 3, methoxyl).

Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.50; H, 6.01. Found: C, 83.27; H, 5.86.

Preparation of 1,4-Bis(α-hydroxybenzyl)benzene.—*p*-Dibenzoylbenzene (11.4 g, 4 mmol) in approximately 300 ml of tetrahydrofuran was added slowly to a stirred suspension of 2 g of lithium aluminum hydride (Alfa Inorganics, Beverly, Mass.) in 100 ml of tetrahydrofuran. The reaction mixture was refluxed for 1 hr. The excess $LiAlH_4$ was then destroyed by cautiously adding 30 ml of water in 100 ml of tetrahydrofuran. The reaction mixture was poured into 1 l. of cold 10% sulfuric acid and stirred 30 min. The product was extracted with chloroform, the organic phase washed with water and 10% sodium bicarbonate solution and dried over anhydrous sodium sulfate, and the solvent removed under vacuum. The crystalline residue (11.2 g, 97%) was dissolved in ethanol from which the two diastereoisomers were obtained by fractional crystallization. Two isomers were thus obtained (A and B).

A: mp 170–172°; infrared (KBr) 3250 cm^{-1} (OH); pmr (acetone-d_6, 45°) τ 2.68 (s, 14, aromatic), 4.20 (d, 2, methine), 5.88 (d, 2, hydroxyl).

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.32; H, 6.25.

B: mp 141–143°; infrared (KBr) 3300 cm^{-1} (OH); pmr (acetone-d_6, 25°) τ 2.69 (s, 14, aromatic), 4.25 (d, 2, methine), 5.40 (d, 2, hydroxyl).

Anal. Found: C, 82.67; H, 6.25.

Preparation of 1,4-Bis(α-methoxybenzyl)benzenes (17).—The methylation technique described by Gillis[19] was applied individually to the two isomers of 1,4-bis(α-hydroxybenzyl)benzene. To 4.5 g of powdered sodium hydroxide in approximately 65 ml of dimethyl sulfoxide was added 3.6 g (12.4 mmol) of the diol and then 45 g (317 mmol) of methyl iodide. The mixture was stirred at room temperature for 1 hr. It was then poured into water, the product extracted with chloroform, the organic phase washed with water and dried over anhydrous sodium sulfate, and the solvent removed under vacuum. The 4-g residue (~100%) crystallized on standing overnight. Recrystallization from 2-propanol yielded two diols (C and D).

C from A, mp 170–172°: mp 98–100°; pmr τ 3.7 (s, 14, aromatic), 4.78 (s, 2, methine), 6.66 (s, 6, methoxyl).

Anal. Calcd for $C_{22}H_{22}O_2$: C, 82.98; H, 6.97. Found: C, 82.83; H, 6.93.

D from B, mp 141–143°: mp 65–67°; pmr τ 2.7 (s, 14, aromatic), 4.78 (s, 2, methine), 6.66 (s, 6, methoxyl).

Anal. Found: C, 82.83; H, 7.02.

Registry No.—**3**, 31020-17-4; **4**, 31020-18-5; **5**, 31024-80-3; **9**, 31024-81-4; **10**, 31024-82-5; **11**, 31024-83-6; **12**, 31024-84-7; **13**, 31024-85-8; **14**, 31024-86-9; (±)-**17**, 31024-87-0; *meso*-**17**, 31024-88-1; **18**, 31020-19-6; 1-benzoyl-4-(α-hydroxybenzyl)benzene, 31020-20-9; (±)-1,4-bis(α-hydroxybenzyl)benzene, 31024-89-2; *meso*-1,4-bis(α-hydroxybenzyl)benzene, 31024-90-5.

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[19] R. G. Gillis, *Tetrahedron Lett.*, 1413 (1968).