distilled and the residue was chromatographed as described for the preparation above, yielding 0.110 g (0.45 mmol) of **4**, 0.417 g (2.24 mmol) of **3**, and 1.796 g (9.54 mmol) of **2**.

C. Uv Irradiation.—A homogeneous solution of 1.35 g (7.33 mmol) of S_4N_4, 200 ml of benzene, and 4.15 g (31.39 mmol) of tetrahydronaphthalene was irradiated for 206 hr at room temperature. After removal of the solvent under vacuum at room temperature, the residue was chromatographed. In addition to the unreacted tetrahydronaphthalene, 0.256 g (1.36 mmol) of **2** and 0.067 g (0.36 mmol) of **3** were obtained. Compound **4** was recovered in traces and identified by tlc analysis.

Reaction of S_4N_4 with 2.—A 0.748-g (3.97 mmol) sample of **2** in 20 ml of xylene was treated with 1.10 g (5.97 mmol) of S_4N_4 and the mixture was refluxed for about 8 hr under nitrogen atmosphere with stirring. After removal of the solvent by distillation at 20 Torr, the residue was chromatographed, yielding 0.059 g (0.24 mmol) of **4**, 0.229 g (1.23 mmol) of **3**, and 0.469 g (2.49 mmol) of **2**.

Reaction of 2 with Sulfur.—A mixture of 0.109 g (0.58 mmol) of **2** and 0.022 g (0.69 mmol) of sulfur was heated at 250–270° for 2.5 hr. After cooling the residue gave after crystallization from methanol 0.078 g (0.42 mmol) of **3**.

Registry No.—**1**, 1143-73-3; **2**, 34910-55-9; **3**, 233-68-1; **4**, 34910-56-0; **5**, 28950-34-7; 9,10-dihydrophenanthrene, 776-35-2; tetrahydronaphthalene, 119-64-2.

Acknowledgment.—This work was supported by C. N. R., Roma, Italy.

New Precursors for Arylcarbenes. Photocycloelimination Reactions of Cyclic Sulfites[1,2]

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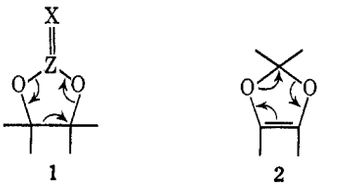
Cyclic arylpinacol sulfites are found to undergo [5 → 2 + 2 + 1] photocycloeliminations to give arylcarbenes in addition to other products. The sulfites studied include benzopinacol sulfite, fluorenopinacol sulfite, *meso*- and *dl*-hydrobenzoin sulfites, and methyl-substituted hydrobenzoin sulfites. With the exception of fluorenopinacol sulfite all fragment to give carbenes and have synthetic utility. Arylcarbenes formed by photolysis of these substrates when generated in methanol give methyl ethers and the transient obtained by photolysis of *meso*- and *dl*-hydrobenzoin sulfites is shown to be virtually identical in properties with that obtained from conventional precursors such as *trans*-2,3-diphenyloxirane and phenyldiazomethane; *i.e.*, the secondary to primary insertion selectivity in pentane and the high stereoselectivity of addition to *cis*-2-butene are the same for phenylcarbene generated from the hydrobenzoin sulfites, 2,3-diphenyloxirane and phenyldiazomethane. The observed lack of dependence of chemical behavior on precursor structure suggests that free phenylcarbene is involved in each case. [5 → 3 + 2] cycloelimination to sulfur trioxide and substituted stilbenes appears to be a competitive process. Under the reaction conditions the stilbenes undergo a secondary reaction, namely cyclization to phenanthrenes. In addition, 1,2-aryl migrations, preceded or accompanied by loss of sulfur dioxide, also compete with cycloelimination. The rearrangements are shown to occur with retention of the substitution patterns on the aryl groups. Thermal reactions of the cyclic sulfites have also been studied and a comparison of the sulfite photo- and thermochemistry made. Possible mechanisms are discussed.

An increasing number of photocycloelimination reactions leading to carbenes have appeared in the literature and these reactions have been surveyed recently.[4] Their thermal counterparts are also the subject of a recent review.[5] In continuing efforts to broaden the scope and synthetic utility of photocycloelimination reactions for the preparation of arylcarbenes, several precursors of the type shown in the general structures **1** and **2** have been investigated.[2,6,7] Substrates of the type **1** were selected for evaluation in cycloelimination studies because of their ready accessibility from the corresponding diols, which themselves may be prepared under reductive conditions. Consequently, such reagents would complement the existing oxirane



1 **2**

carbene precursors which in general are formed oxidatively.[8]

In previous investigations we have established that many vicinal diaryl-substituted heterocyclic systems undergo photocycloelimination to give arylcarbenes.[6,7,8] *A priori*, one might expect that systems such as **1** and **2** undergo cycloelimination reactions in the [5 → 2 + 2 + 1] and [5 → 4 + 1] modes, respectively, and indeed members of these classes behave as anticipated.[9]

For example, *trans*-4,5-diphenyl-4,5-dicyano-1,3,2-dioxa-P^V-phospholane (**3**), a system structurally related to **1**, undergoes [5 → 2 + 2 + 1] cycloelimination as

(1) We gratefully acknowledge financial support of this research from the National Science Foundation (Grants GP 9434 and GP 28171) and The Petroleum Research Fund (Grant PRF 5471).

(2) For preliminary communications on this and related work see (a) R. L. Smith, A. Manmade, and G. W. Griffin, *J. Heterocycl. Chem.*, **6**, 443 (1969); (b) R. L. Smith, A. Manmade, and G. W. Griffin, *Tetrahedron Lett.*, 663 (1970).

(3) Abstracted in part from the Ph.D. Dissertation of A. Manmade, Louisiana State University in New Orleans, 1971.

(4) G. W. Griffin, *Angew. Chem.*, **83**, 604 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 537 (1971).

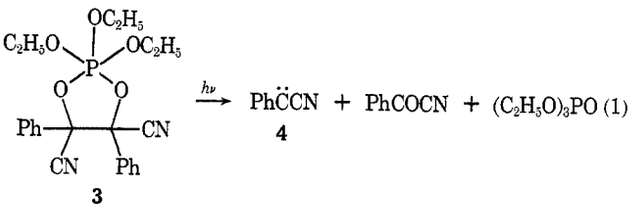
(5) R. W. Hoffmann, *Angew. Chem.*, **83**, 595 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 529 (1971).

(6) P. Petrellis and G. W. Griffin, *Chem. Commun.*, 1099 (1968).

(7) R. M. G. Nair, E. Meyer, and G. W. Griffin, *Angew. Chem.*, **80**, 442 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 462 (1968).

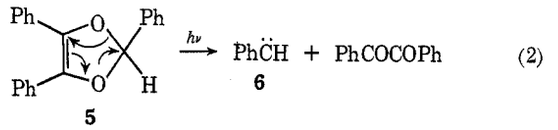
(8) For the latest papers in the oxirane series see (a) R. S. Becker, R. O. Bost, J. Kolc, N. R. Bertoniere, R. L. Smith, and G. W. Griffin, *J. Amer. Chem. Soc.*, **92**, 1302 (1970); (b) N. R. Bertoniere, S. P. Rowland, and G. W. Griffin, *J. Org. Chem.*, **36**, 2956 (1971).

(9) We shall employ the convention suggested by R. Huisgen [*Angew. Chem.*, **80**, 329 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 321 (1968)] in which cycloadditions and cycloeliminations are classified on the basis of the size of the ring formed or destroyed and the number of ring members contributed to each fragment.

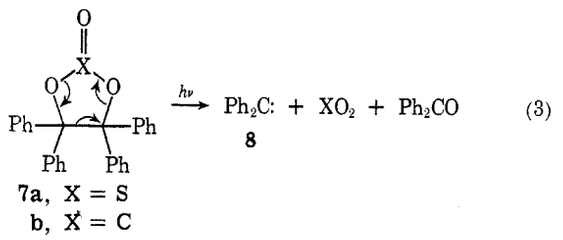


indicated in eq 1 to give phenylcyanocarbene (**4**), benzoyl cyanide, and triethyl phosphate.[6]

In the case of substrates such as **2** the carbene is extruded with formation of a diketone, as exemplified by the photoconversion of 2,4,5-triphenyl-1,3-dioxole (**5**) to phenylcarbene (**6**) and benzil (eq 2).[7] For convenience the cycloelimination reactions are formulated mechanistically in a concerted fashion, although intermediates have not been excluded and in fact may be involved in several cases.[4,8]



On the basis of the reactions cited above and related examples,[7,10] it was felt that suitably substituted cyclic sulfites such as **7a** or carbonates **7b** also should undergo [5 → 2 + 2 + 1] photocycloeliminations to give arylcarbenes such as **8** as depicted in eq 3. While this

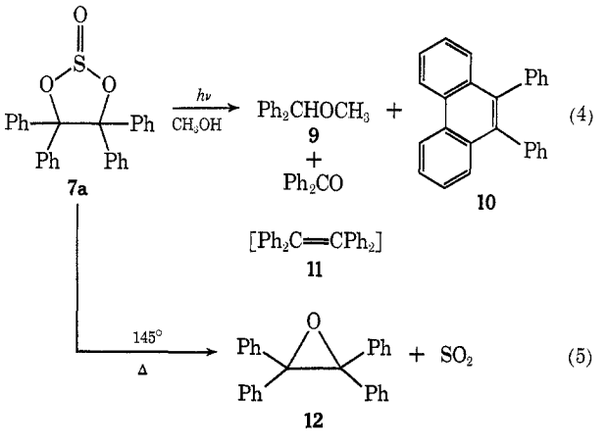


paper is restricted to a discussion of the photochemistry of sulfites related to **7a**, the photolytic behavior of carbonates such as **7b** also has been investigated extensively[2] and will be the subject of a future full communication.

Results and Discussion

Benzopinacol sulfite (**7a**), a cyclic sulfite incorporating the desired structural prerequisites, was selected as a substrate for our preliminary photocycloelimination studies in this area since the anticipated carbene, diphenylcarbene (**8**), has been studied extensively both chemically[11] and spectroscopically.[12,13a] Kirmse, Hörner, and coworkers[11] have established that diphenylcarbene obtained photolytically from diphenyldiazomethane is nucleophilic in character and is readily protonated in alcohols to give the benzhydryl carbonium ion, which subsequently solvolyzes to give benzhydryl ethers. Consequently, for this as in previous studies,[2,6,7] methanol was selected as a solvent trapping agent in initial screening studies of potential carbene precursors.

Benzopinacol sulfite (**7a**) is conveniently synthesized by a modification of the procedure employed for hydrobenzoin sulfites described by Thompson and coworkers[14] consisting of addition of thionyl chloride in methylene chloride to a solution of benzopinacol and pyridine in methylene chloride. Upon irradiation (254 nm) in methanol, benzopinacol sulfite (**7a**) does undergo photocycloelimination to produce diphenylcarbene (**8**), as evidenced by the formation of benzhydrylmethyl ether (**9**) (40%). Other compounds identifiable among the reaction products after separation by thick layer chromatography included benzophenone (15%) and 9,10-diphenylphenanthrene (**10**) (10%) (eq 4).



Tetraphenylethylene (**11**) is known to undergo dehydrophotocyclization to 9,10-diphenylphenanthrene (**10**), a result which suggests that the phenanthrene **10** may in fact be a secondary photoproduct arising from **11**.[15] The formation of **11** from **7a** requires [5 → 3 + 2] cycloelimination with extrusion of sulfur trioxide, since dimerization of diphenylcarbene (**8**) to **11** is a process not generally observed in solution at ambient temperatures.[16] That sulfur dioxide is formed upon photolysis of **7a** was confirmed by infrared and mass spectroscopic examination of an aliquot of the effluent gas. It is noteworthy that tetraphenyloxirane (**12**) could not be detected by thin layer chromatography among the photoproducts of **7a** even at low conversions. Consequently, prior oxirane formation and subsequent fragmentation appears an unlikely primary source of **8**, at least at ambient temperature, since the relative extinction coefficients for **7a** and **12** are such that a steady state concentration of **12** sufficient for detection would be required for competitive cycloelimination.

In contrast to the photochemical behavior, benzopinacol sulfite (**7a**) does give tetraphenyloxirane (**12**) upon thermolysis at 145° in essentially quantitative yield (eq 5), and no rearrangement products which might have been anticipated on the basis of the photochemistry of related sulfite substrates (*vide infra*) were detected. The theoretical implications of these contrasting photo- and thermochemical results are presently under study.

Fluorenopinacol sulfite (**13**), which is structurally re-

(10) C. Bischoff and H. Brandtstaedter, *Monatsber. Deut. Akad. Wiss. Berlin*, **8**, 888 (1966); *Chem. Abstr.*, **68**, 68222*h* (1968).

(11) W. Kirmse, L. Hörner, and H. Hoffmann, *Justus Liebigs Ann. Chem.*, **614**, 19 (1958); W. Kirmse, *ibid.*, **666**, 9 (1963).

(12) R. S. Becker, J. Kolc, R. O. Bost, H. Dietrich, P. Petrellis, and G. W. Griffin, *J. Amer. Chem. Soc.*, **90**, 3292 (1968).

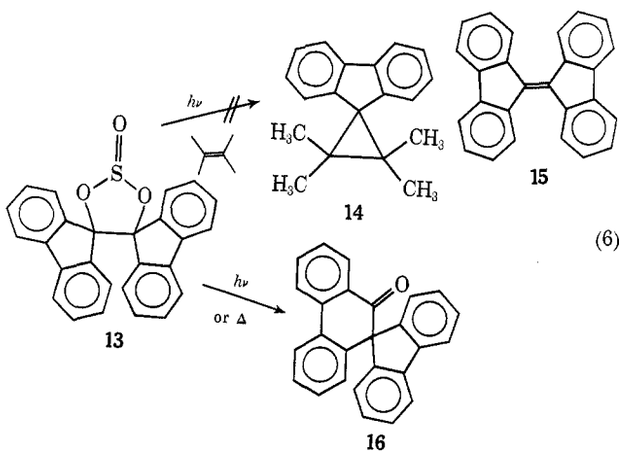
(13) (a) E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, *J. Chem. Phys.*, **40**, 2408 (1964); (b) H. Kristinsson and G. W. Griffin, *J. Amer. Chem. Soc.*, **88**, 1579 (1966).

(14) Q. E. Thompson, M. M. Crutchfield, and M. W. Dietrich, *J. Org. Chem.*, **30**, 2696 (1965).

(15) M. V. Sargent and C. J. Timmons, *J. Chem. Soc.*, 5545 (1964).

(16) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 83.

lated to **7a**, was examined as a potential source of fluorenylidene, a species for which a limited number of shelf-stable precursors exist.[17] Substantial difficulty was encountered in the preparation of the corresponding bisfluorenylidene oxide,[18] which by analogy with other oxiranes should undergo [3 → 2 + 1] cycloelimination to fluorenylidene and fluorenone. In contrast the sulfite **13** was readily synthesized from fluorenopinacol in a manner similar to that described above for **7a**, and found to be stable when stored in a dark bottle at 5°. Upon irradiation (350 nm) in 2,3-dimethyl-2-butene, **13** undergoes photofragmentation to give sulfur dioxide; however, efforts to detect any of the anticipated 2,2,3,-3-tetramethylspiro[cyclopropane-1,9′-fluorene] (**14**) have proved unrewarding. Furthermore, the photostable, bright red bisfluorenylidene (**15**), a potential



(6)

[5 → 3 + 2] cycloelimination fragment, was conspicuously absent among the photoproducts.

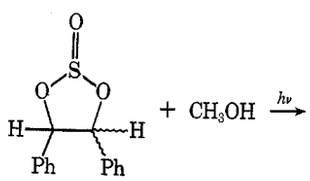
The principal photoproduct obtained from **13** is 9-diphenylenephenanthrone (**16**) formed by 1,2-aryl migration accompanied or preceded by elimination of sulfur dioxide. Furthermore, the spiro ketone **16** is the primary thermolysis product obtained from **13** at 145° and also has been obtained by both photolysis and thermolysis of the corresponding phosphorane.[6,19]

It is evident from the results cited above that the sulfites **7a** and **13** differ markedly in their respective modes of photofragmentation despite their structural similarities. In the case of **7a** cycloelimination is observed to give primarily diphenylcarbene (**8**). Formation of sulfur trioxide and 9,10-diphenylphenanthrene appears to be a competing reaction of secondary importance. In contrast, rearrangement to the spiro ketone **16** is the only significant photoreaction observed with **13** under the reaction conditions employed. In addition, a marked difference in their thermal behavior is also apparent; while similar thermolysis and photolysis products are obtained from **13**, such is not the case with **7a**. The reasons for these differences in behavior remain to be established.

In an attempt to characterize chemically carbenes produced as a result of photocycloelimination reactions of sulfites and to compare and contrast the properties of these species with those generated from other sources, a study of the hydrobenzoin sulfites (**17** and **18**, respectively) was initiated.[20] With these substrates it was also possible to investigate the effect of sulfite stereochemistry on the cycloelimination process by comparing the diastereomeric *meso*- and *dl*-pinacol sulfites (**17** and **18**, respectively).

The sulfites **17** and **18** were prepared by treatment of the corresponding hydrobenzoins with thionyl chloride according to the procedure given by Thompson, *et al.*[14] These investigators noted that geometrical isomerism is possible in the case of **17** as a result of the tetrahedral geometry assumed by the sulfur atom in the system. Two forms differing in the orientation of the exocyclic oxygen atom are isolable at 25°. The major and minor isomers are distinguishable by pmr spectroscopy and for convenience the major isomer has been used in these studies; however, photoequilibration of the isomeric sulfites **17** prior to cycloelimination has not been excluded.

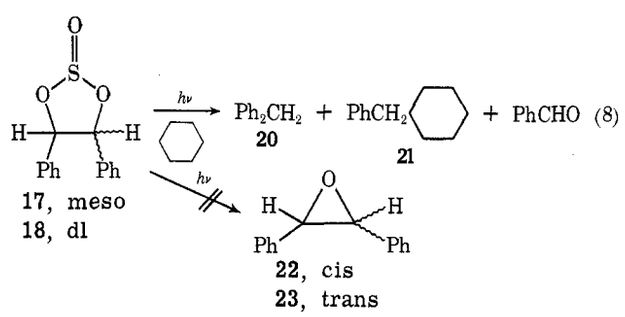
Preliminary chemical proof that phenylcarbene (**6**) is formed in the photocycloelimination reactions of the sulfites **17** and **18** was obtained by irradiating (254 nm) these substrates in methanol. As expected, benzylmethyl ether (**19**), sulfur dioxide, and benzaldehyde as well as diphenylmethane (**20**) are obtained from the photolysis mixtures of **17** and **18** (eq 7). Benzaldehyde



$$\underset{\textbf{19}}{PhCH_2OCH_3} + SO_2 + \underset{\textbf{20}}{Ph_2CH_2} + PhCHO \quad (7)$$

and diphenylmethane (**20**) were separated by preparative gas chromatography and their identity was established by comparison with authentic samples.

Irradiation (254 nm) of **17** or **18** in cyclohexane gave, as anticipated, the insertion product benzylcyclohexane (**21**) in high yield in addition to sulfur dioxide, benzaldehyde, and diphenylmethane (**20**) (eq 8). While the



(8)

mechanism of formation of **20** will be discussed later, it is significant that under the reaction conditions investigated no oxiranes are detected, *i.e.*, *cis*-2,3-diphenyloxirane (**22**) in the case of **17** or *trans*-2,3-diphenyloxirane (**23**) in the case of **18**, when the photoreactions were monitored using pmr and thin layer chromatographic techniques. Furthermore, the absence of detectable amounts of stilbene and its dehydrophotocy-

(17) Reference 16, p 87.
(18) E. Bergmann and J. Hervey, *Chem. Ber.*, **62**, 893 (1929).
(19) F. Ramirez and C. P. Smith, *Chem. Commun.*, 662 (1967).
(20) H. Dietrich, G. W. Griffin, and R. C. Petterson, *Tetrahedron Lett.*, 153 (1968).

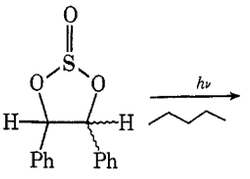
clization product phenanthrene among the reaction products indicates that [5 → 3 + 2] photocycloelimination does not occur to a significant extent with either **17** or **18**. This is in contrast to the behavior exhibited by **7a**, where formation of sulfur trioxide and 9,10-diphenylphenanthrene (**10**) competes with cycloelimination to give the carbene **8**. It is noteworthy that in this respect **17** and **18** behave in a manner similar to fluorenopinacol sulfite (**13**). Unlike **13**, however, the sulfites **17** and **18** were found to be photostable when irradiated in Pyrex vessels at 350 nm and could be recovered quantitatively in each case.

Although it is apparent from the chemical data that both **17** and **18** undergo [5 → 2 + 2 + 1] cycloeliminations to produce "free" carbene, the characteristic phenylcarbene epr signal could not be observed upon photolysis of these substrates for reasons yet undetermined.[21] Similar results were observed for 2,3-diphenyloxirane (**23**) and triphenyloxirane where no epr signal was detected for phenylcarbene (**6**) despite convincing chemical evidence to the contrary for its formation.[20,21] In the absence of direct epr and/or optical spectroscopic data, it was necessary to obtain further chemical proof for the contention that **17** and **18** are indeed phenylcarbene precursors.

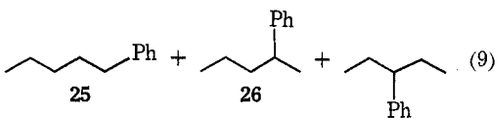
Competitive insertion experiments prove particularly useful as a method for comparing divalent carbon species generated from different sources such as **17** and **18**.[20,22] Gutsche and coworkers[22] have previously determined the insertion selectivity of phenylcarbene (**6**) generated from phenyldiazomethane (**24**). Additional data on the selectivity of **6** formed from the oxiranes **22** and **23** and the diazo compound **24** were reported by Griffin and coworkers.[20] A similar study was initiated of the insertion selectivity of **6** generated from the sulfites **17** and **18** and the conventional precursors **23** and **24** into primary and secondary C–H bonds of pentane.

Equimolar solutions of the compounds under study were made in *n*-pentane and photolyzed (254 nm) simultaneously under identical conditions using the "merry-go-round" technique in order to ensure uniform exposure. Insertion product ratios were determined gas chromatographically employing *n*-amylbenzene as an internal standard. Absolute yields were obtained by determination of the gas chromatographic response factors utilizing authentic mixtures of known concentration of the internal standard and reaction products. To ensure that the results obtained reflect initial insertion rates, relatively short irradiation times (25 min) were employed and the number of lamps in the light source was adjusted from 16 to 8 to reduce the light flux to a desired level.

In a typical case the three insertion products **25**, **26**, and **27** were obtained from *dl*-hydrobenzoin sulfite (**18**) (eq 9) and the relative ratios of these products were found to be 1.00:5.95:2.10, respectively. The ratio of the combined amounts of 2- and 3-benzylpentanes (**26** and **27**, respectively, formed by insertion into the six secondary C–H bonds) to 1-phenylhexane (**25**) (produced by attack at the six primary C–H bonds) was established from several determinations as 8.00 ± 0.16



17 or 18

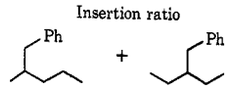
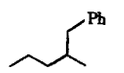


25 26 27 (9)

(see Table I). The ratio of 2- to 3-benzylpentanes correspondingly is 2.90 ± 0.04, which when statistically corrected gives a selectivity factor for C_2H or C_4H over C_3H (all secondary) of 1.45 ± 0.05.

TABLE I

C–H INSERTION SELECTIVITY OF PHENYLCARBENE

Phenylcarbene precursor	Yields, % (254 nm, 8 lamps, 25 min)	Insertion ratio 	Insertion ratio[c] 
17	5.5	8.48 ± 0.24[a]	1.41 ± 0.05[a]
18	6.6	8.00 ± 0.18	1.45 ± 0.02
23	45.5	8.33 ± 0.14	1.35 ± 0.04
24	31.5	7.14 ± 0.14	1.31 ± 0.09
	18.3[b]	8.38 ± 0.19	1.33 ± 0.09

[a] Limits of error in all cases are standard deviations obtained on multiple integrations of several chromatograms. [b] 350 nm; 16 lamps; 4 hr. [c] Relative ratios corrected for number of hydrogens.

The results obtained in all cases substantiate the original proposal that the photolysis of cyclic sulfites may in fact give rise to species virtually indistinguishable chemically from those produced from conventional carbene precursors such as *trans*-2,3-diphenyloxirane (**23**) and phenyldiazomethane (**24**). Higher yields are obtained with the oxirane **23** and the diazo precursor **24** (Table I), which indicates that the rate of fragmentation of **23** (and **22**) exceeds that of **17** and **18**. It remains to be determined if the quantum yield is higher for the former pair or if the difference in rate is only a reflection of their higher extinction coefficients (Table II). The sulfites presently under examination do, of course, afford significantly higher yields of insertion products upon prolonged irradiation and are of preparative value; however, preservation of the initial selectivity factors was, of course, of paramount importance in the present study.

The stereochemistry of the cyclic sulfite precursors **17** and **18** exerts little or no influence upon the observed insertion selectivity factors, although the initial fragmentation rates for the *dl* isomer **18** may be slightly higher. This is not unexpected in view of the higher extinction coefficients observed for this diastereomer (Table II). The extinction coefficients differ significantly at 264 nm and studies are in progress to establish whether at this wavelength precise measurement of relative cycloelimination rates is feasible. Analysis of the reaction mixture at low conversions (10%) where

(21) We wish to thank Dr. Trozzolo and coworkers for their attempts to obtain the desired epr spectra.

(22) C. D. Gutsche, G. L. Bachman, and R. S. Coffey, *Tetrahedron*, **18**, 617 (1962).

TABLE II
ULTRAVIOLET SPECTRAL DATA FOR CYCLIC SULFITES

Sulfite	λ_{max}, nm[a]	ϵ
Benzopinacol (**7a**)	266	968
	261	1,031
	254	906
Fluorenopinacol (**13**)	288	14,700
	278	17,700
	269	16,100
	239	59,000
	232	56,400
meso-Hydrobenzoin (**17**)	268 sh	225
	264	398
	258	474
	252	396
dl-Hydrobenzoin (**18**)	269	292
	263	470
	257	502
	252	373
meso-4,4′-Dimethylhydrobenzoin (**36**)	273	322
	268	407
	263	576
	257	485
meso-2,2′-Dimethylhydrobenzoin (**37**)	273	687
	266	786
	260	620
meso-α,α'-Dimethylhydrobenzoin (**40**)	264	396
	258	504
	252	420
dl-α,α'-Dimethylhydrobenzoin (**41**)	263	388
	257	477
	252	366

[a] Determined in 90% ethanol.

shielding of the alternate isomer, if formed, should be relatively effective shows that within the limits of detectability (pmr and tlc) interconversion of the two diastereoisomers **17** and **18** does not occur. The presence of oxygen has no apparent effect on the selectivity factors exhibited by the carbenes generated photolytically from **17** and **18**. Neither *cis*- nor *trans*-2,3-diphenyloxirane (**22** nor **23**, respectively) could be detected among the reaction products by tlc. These results suggest that a stepwise mechanism involving the oxirane as an intermediate in the photolysis is improbable here as in the case of **7a**.

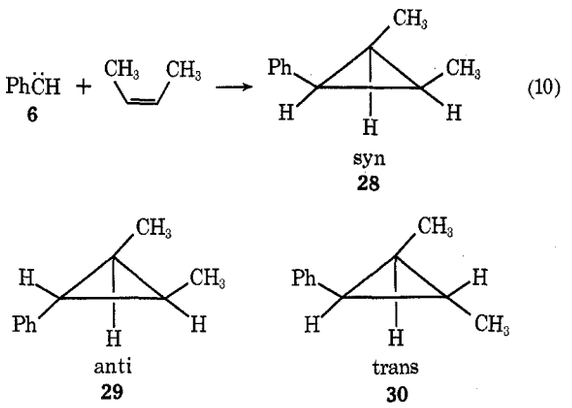
It is evident from the data presented in Table I that species showing similar discriminatory behavior are involved in the insertion reactions of **17**, **18**, **22**, and **23**. The lack of dependence of the insertion ratios on the prior history of the carbene may be interpreted in at least two ways: (a) the reaction is insensitive to energetic factors, *i.e.*, requires no activation energy which is unlikely, and/or (b) regardless of source, the carbenes formed are isoenergetic. Intuitively it is unreasonable that *nascent* phenylcarbene generated from such dissimilar precursors as oxiranes, sulfites, and diazo compounds should be isoenergetic, but perhaps thermal equilibration to a common vibrational level of the same state may be occurring prior to insertion. It is also interesting that the reactivity of the carbene from phenyldiazomethane (**24**) is affected by the nature of the radiation source as seen in Table I. Phenylcarbene (**6**) generated from **24** using a 254-nm source exhibits lower selectivity than that produced at a longer incident wavelength (>300 nm). Further speculation on the origin of these effects is unwarranted at this time in the absence of additional data, although it is noteworthy in this connection that the proportion of ground triplet state methylene produced in the primary photolysis of diazomethane is independent of wavelength at least over the range from 366 to 436 nm.[23]

Extensive effort has been devoted to characterizing the multiplicity of the reactive state(s) of phenylcarbene (**6**). A triplet ground state has been assigned to **6** on the basis of epr[13] and optical[8a] matrix isolation techniques. Calculations of the extended Hückel type support these experimental observations;[24] however, it is generally accepted that C–H insertion reactions of phenylcarbene involve a direct single step mechanism requiring the singlet state which reacts with the substrate more rapidly than interconversion occurs to the triplet ground state.[25,26] Furthermore, it is widely conceded that the stereochemistry of addition of phenylcarbene generated from a wide variety of precursors[20,23,27] is more easily rationalized on the basis of a singlet rather than a triplet mechanism; *i.e.*, when phenylcarbene reacts with an unsymmetrically substituted alkene such as 2-butene the stereochemical integrity of the alkene is maintained and high stereoselectivity (>95%) is observed.[22,27] Such results can only be accommodated by a triplet mechanism if the intermediate trimethylene diradical demanded by spin considerations undergoes cyclization at a rate sufficiently fast to preclude extensive rotamer equilibration; *i.e.*, the spin-imposed barrier to bond formation in the triplet state is surmounted by rapid intersystem crossing to the triplet state. In a recent reexamination of the phenylcarbene–2-butene reactions Moss and Dolling have demonstrated that less specific cyclopropanation occurs and increased abstraction recombination processes intervene when photolyses are conducted in frozen *cis*-butene matrices.[28] Although other explanations also are advanced it is inviting to accept their proposal that initially singlet carbene is formed but restricted in the matrix decays to the triplet ground state at a rate which is at least comparable with stereospecific addition to the matrix.

Since measurement of the discrimination exhibited by phenylcarbene (**6**) in the possible modes of addition to *cis*-2-butene (eq 10) has been widely employed as a sensitive method of comparing the properties of this species when generated from different sources, we have extended these studies to the cyclic sulfite substrates **17** and **18**.

Irradiations of equimolar amounts of **17**, **18**, **23**, and **24** were conducted in quartz Griffin–Worden pressure vessels[29] in *cis*-2-butene at 254 nm. The photolysis mixtures were analyzed by glc and the isomeric cyclopropanes **28**, **29**, and **30** were identified by comparison with authentic samples obtained by similar preparative scale photolysis. The identities of these cyclopropanes previously had been established by examination of the

(23) G. W. Taylor and J. W. Simons, *Can. J. Chem.*, **48**, 1016 (1970).
(24) R. Hoffmann, G. D. Zeiss, and G. W. VanDine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968).
(25) W. v. E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **83**, 1989 (1961).
(26) P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956).
(27) (a) G. L. Closs, R. A. Moss, and J. J. Coyle, *J. Amer. Chem. Soc*, **84**, 4985 (1962); (b) G. L. Closs and R. A. Moss, *ibid.*, **86**, 4042 (1964).
(28) R. A. Moss and U.-H. Dolling, *ibid.*, **93**, 954 (1971).
(29) Kontes of Illinois, Evanston, Ill.; Worden Quartz Products, Inc., Houston, Tex.



(10)

pmr chemical shifts of the methyl protons and thus were readily identified from literature data.[27] The reactions were conducted using shorter irradiation times than those employed in the pentane insertion studies (*vide supra*) in order to preclude photoisomerization of the photolabile cyclopropanes subsequent to addition.[30-33] The reactions are highly stereoselective in each case (>95%) and from results of the comparative studies delineated in Table III it is clear that the

TABLE III

STEREOSELECTIVITY OF ADDITION OF PHENYLCARBENE FROM DIVERSE SOURCES TO *cis*-2-BUTENE

Phenylcarbene precursor	Syn:anti ratio[a]
17	1.17 ± 0.01
18	1.16 ± 0.01
23	1.19 ± 0.01
24	1.17 ± 0.01

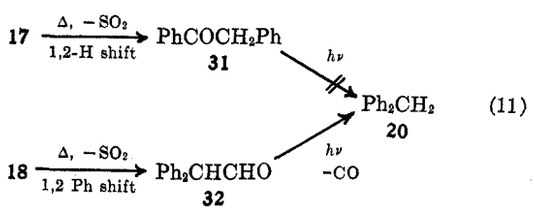
[a] Limits of error in all cases are standard deviations based on multiple integrations of several gas chromatograms.

stereochemistry of addition (syn/anti ratio) is essentially invariant regardless of source and in agreement with results previously reported by Closs and Moss.[27] In light of these factors and the comparative C–H insertion data (*vide supra*) little doubt remains that a common intermediate is involved which we believe is "free" phenylcarbene on the basis of the independence of chemical behavior on precursor structure. It must be assumed that phenylcarbene (**6**) is formed in the singlet state and adds to *cis*-2-butene faster than intersystem crossing to the triplet ground state can occur. However, it appears that a small amount of competitive intersystem crossing to triplet phenylcarbene must be occurring, since 2–5% of *trans*-2,3-dimethyl-1-phenylcyclopropane (**30**) has been observed in all cases studied. It is believed that this is a primary product of addition and not the result of subsequent product isomerization, since the major primary products, cyclopropanes **28** and **29**, were found to be stable to the reaction conditions provided irradiation times are not prolonged (>9 min).

The observed predominance of the least stable syn isomer **28** in each case was first reported by Closs and coworkers[26] and confirmed by Griffin and Kristinsson.[31] A mechanistic interpretation of this phenomenon was advanced previously by Closs and coworkers.[27] It is proposed that a favorable transition state develops for syn addition in which the polarizable aryl electrons interact by London dispersion forces with the cis olefinic alkyl substituents.

The thermal behavior of the hydrobenzoin sulfites parallels that observed for fluorenopinacol sulfite (**13**) rather than benzopinacol sulfite. Price and Berti[34a] observed that **17** and **18** upon thermolysis at 240° do not form the corresponding oxiranes **22** and **23**, but undergo conversion to deoxybenzoin (**31**) and diphenylacetaldehyde (**32**), respectively, in excellent yields. Similar results have recently been reported by Coxon and coworkers[34b] and confirmed in our laboratories. Bridged zwitterionic Ar_i-3[35] mechanisms leading to enol sulfite intermediates are proposed to rationalize these conversions. The enol sulfites may then undergo concerted or stepwise collapse to the observed products.

The isolation of the common photoproduct diphenylmethane (**20**) from the hydrobenzoin sulfites **17** and **18** also must be rationalized. In light of the thermochemistry of **17** and **18** it appeared likely that either **31** and/or **32** might be reasonable precursors for **20**. In independent experiments it was demonstrated that diphenylacetaldehyde (**32**) (a product of 1,2-phenyl migration) does undergo photodecarbonylation under the reaction conditions to give diphenylmethane (**20**).[8a,36] The formation of **32** from the sulfites **17** and **18** in a primary photochemical step is not unexpected in light of the previously reported analogous interconversion of fluorenopinacol sulfite (**13**) to the spiro ketone **16**, which also requires 1,2-phenyl migration. Deoxybenzoin (**31**) (a product of 1,2-H migration) in contrast is not converted to **20**, but as previously reported photolyzes to give mainly benzaldehyde and 1,2-diphenylethane.[37] Therefore **31** may be excluded as a source of **20** in the photofragmentation of **17** and **18**. This is also supported by the fact that we were unable to detect more than trace amounts of **31** by capillary gas chromatographic analysis of the irradiation mixtures of **17** and **18**. Our inability to detect substantial quantities of **32** is attributed to the extreme photolability of this aldehyde.



(11)

1,2-Phenyl migration is a process which is not without precedent in excited-state chemistry. For example, we have shown that 1,1,3,3-tetraphenylpropene is transformed into 1,1,2,3-tetraphenylcyclopropane, the product of photocyclization accompanied by phenyl mi-

(30) H. Kristinsson and G. W. Griffin, *J. Amer. Chem. Soc.*, **88**, 378 (1966).

(31) H. Kristinsson and G. W. Griffin, *Tetrahedron Lett.*, 3259 (1966).

(32) P. H. Mazzocchi, R. S. Lustig, and G. W. Craig, *J. Amer. Chem. Soc.*, **92**, 2169 (1970); G. W. Griffin and E. Waldau, unpublished results.

(33) E. W. Yankee and D. J. Cram, *J. Amer. Chem. Soc.*, **92**, 6328 (1970), and references cited therein.

(34) (a) C. C. Price and G. Berti, *ibid.*, **76**, 1211 (1954); (b) J. M. Coxon, M. P. Hartshorn, G. R. Little, and S. G. Maister, *Chem. Commun.*, 271 (1971).

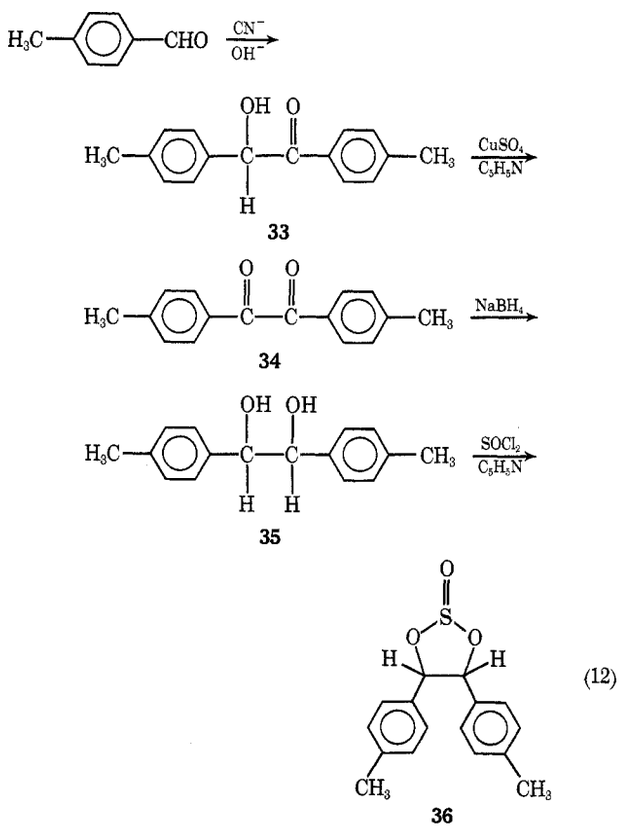
(35) R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3105 (1957).

(36) M. Elam, P. Petrellis, H. Kristinsson, and G. W. Griffin, unpublished results.

(37) A. Schönberg, "Preparative Organic Photochemistry," Springer-Verlag, New York, N. Y., 1968, p 216.

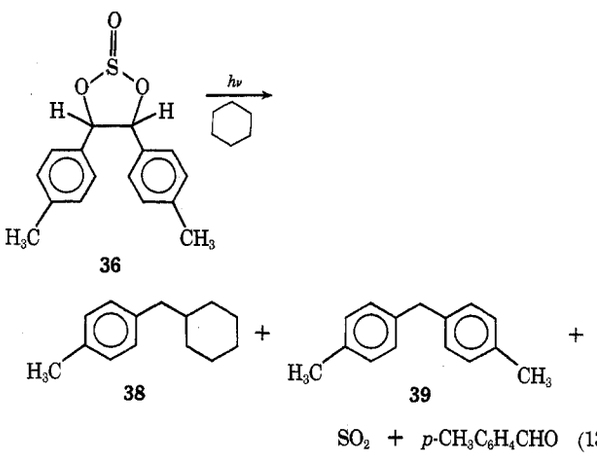
gration to the exclusion of H migration.[38] Preferential phenyl migration also occurs in the photocyclization of 1,1,3-triphenyl-3-methoxypropene to 1,1,2-triphenyl-3-methoxycyclopropane.[39] Other examples of predominance of phenyl over alkyl migration also are known.[40] While photochemical examples of 1,2-hydrogen migration have been reported, such processes are relatively inefficient.[38,41]

In order to determine the nature of the transition state in the photoinduced phenyl migrations observed with **17** and **18**, *meso*-4,4′-dimethylhydrobenzoin sulfite (**36**) and *meso*-2,2′-dimethylhydrobenzoin sulfite (**37**) were synthesized from the respective pinacols and photolyzed. The synthesis of the pinacol **35** was achieved by reduction of *p,p*′-bitolil (**34**) with sodium borohydride. The bitolil **34**, in turn, was obtained by oxidation of the corresponding benzoin **33** prepared from *p*-tolualdehyde, with copper sulfate and pyridine utilizing the method of Clarke and Dreger.[42] *meso*-4,4′-Dimethylhydrobenzoin (**35**) obtained in this way was converted to **36** in the usual manner with thionyl chloride.[14] *meso*-2,2′-Dimethylhydrobenzoin and its sulfite **37** were obtained from *o*-tolualdehyde in a manner analogous to that described for **36** in eq 12.



(12)

Upon irradiation (254 nm) of *meso*-4,4′-dimethylhydrobenzoin sulfite (**36**) in cyclohexane, *p*-tolylcarbene as well as sulfur dioxide and *p*-tolualdehyde are produced, as evidenced by formation of *p*-tolylcyclohexylmethane (**38**). The anticipated ditolylmethane possibly formed by photodecarbonylation of the intermediate rearrangement product, ditolylacetaldehyde, was shown by glc to be primarily the 4,4′-disubstituted isomer **39**, a result which is consistent with an Ar_1-3 transition state proposed for the corresponding thermal conversion (eq 13).[34,43]

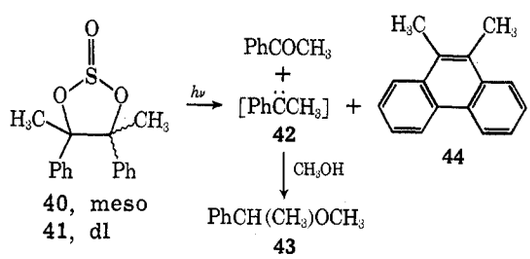


SO_2 + *p*-$CH_3C_6H_4CHO$ (13)

Similarly *meso*-2,2′-dimethylhydrobenzoin sulfite (**37**) upon irradiation (254 nm) in cyclohexane gave the anticipated product *o*-tolylcyclohexylmethane and di-*o*-tolylmethane accompanied by sulfur dioxide and *o*-tolualdehyde, providing further evidence supporting our mechanistic conclusions.

The photolysis of acetophenone pinacol sulfites was also studied in order to determine the effect of alkyl substitution on the cycloelimination reactions of cyclic sulfites and to provide additional precursors for methylphenyl carbenes.[44] The requisite *meso*- and *dl*-α,α'-dimethylhydrobenzoin sulfites (**40** and **41**, respectively) were synthesized in the conventional manner from the corresponding *meso*- and *dl*-α,α'-dimethylhydrobenzoins and thionyl chloride.[14] As anticipated, the sulfites **40** and **41** were found to undergo photocycloelimination upon irradiation (254 nm) to give the expected phenylmethylcarbene (**42**) which in methanol solvolyzes to α-phenethylmethyl ether (**43**) which is readily identified by glc and pmr spectroscopy. Other compounds detected among the photolytic products of **40** and **41** after separation by thick layer chromatography are acetophenone and 9,10-dimethylphenanthrene (**44**) (eq 14).

The formation of **44** suggest that [5 → 3 + 2] cycloelimination takes place with **40** and **41** to give sulfur trioxide and 1,2-dimethylstilbene(s). The latter sub-



(14)

(38) G. W. Griffin, A. P. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965).

(39) J. J. Brophy and G. W. Griffin, *ibid.*, 493 (1970).

(40) H. Kristinsson and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 5968 (1967).

(41) M. Pomerantz and G. W. Gruber, *ibid.*, **89**, 6798 (1967).

(42) H. T. Clarke and E. E. Dreger, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1964, p 87.

(43) The series of six possible isomeric ditolylmethanes have been synthesized and an attempt is presently being made to achieve total glc resolution, which has proved exceedingly difficult. A photolability study similar to that performed on the six isomeric dimethylbiphenyls is contemplated once resolution is achieved which will allow us to set limits on the homogeneity of the ditolylmethanes obtained from **36** and **37**. See U. Mende, J. L. Laseter, and G. W. Griffin, *Tetrahedron Lett.*, 3747 (1970).

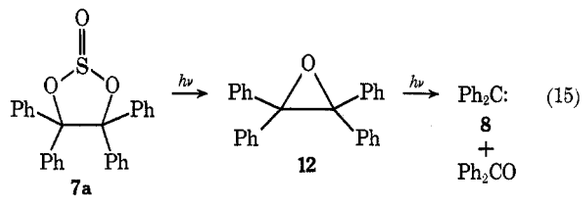
(44) H. Kristinsson, *ibid.*, 2343 (1966).

sequently undergo photodehydrocyclization to 9,10-dimethylphenanthrene (**44**). It was observed that smaller amounts of **44** are formed from **41** than **40**, which may be the case because concerted [5 → 3 + 2] cycloelimination with **41** would give *trans*-1,2-dimethylstilbene, which must undergo geometrical isomerization prior to dehydrocyclization. In contrast to the results obtained with the fluorenopinacol sulfite (**13**) and the hydrobenzoin sulfites (**17** and **18**) no rearrangement products were isolable from the irradiation mixtures obtained from **40** and **41**.

From the data compiled to date on the photochemical behavior of aryl-substituted cyclic sulfites it is apparent that these substrates may undergo [5 → 2 + 2 + 1] photocycloeliminations to carbenes, react in a [5 → 3 + 2] manner to give sulfur trioxide and aryl-substituted alkenes (which in turn under the reaction conditions are converted by photodehydrocyclization to phenanthrenes), and suffer rearrangement involving 1,2-aryl migration preceded or accompanied by loss of sulfur dioxide.

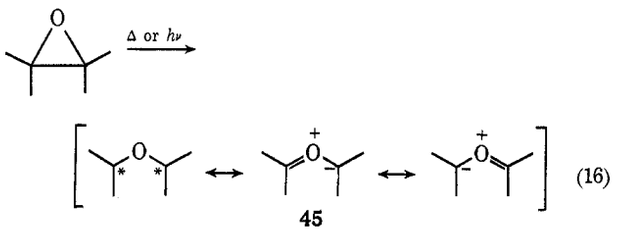
It has been demonstrated that all sulfites studied, with the exception of fluorenopinacol sulfite (**13**), fragment to arylcarbenes. It is evident from comparative C–H insertion selectivity and additional stereochemical studies that phenylcarbene (**6**) formed by cycloelimination from the diastereomeric hydrobenzoin sulfites **17** and **18** is probably singlet in character and identical with that obtained from more conventional precursors such as *trans*-2,3-diphenyloxirane (**23**) and phenyldiazomethane (**24**).

The results of earlier work in this laboratory confirm that suitably substituted oxiranes fragment upon irradiation to carbenes.[4,8] *A priori*, it appeared reasonable that carbene formation from sulfites might occur in a stepwise manner with formation of an oxirane upon loss of sulfur dioxide, which in turn could be the primary carbene precursor. This potential mode of fragmentation is exemplified for benzopinacol sulfite (**7a**) in eq 15. This reaction pathway remains subject



7a (15)

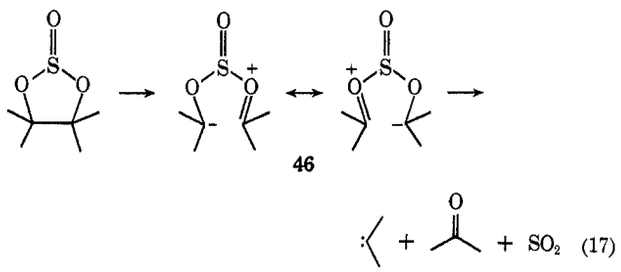
to consideration in view of the known thermal conversions of **7a** to **12** and the observation that the sulfites studied, when irradiated at −196° in a rigid matrix of 2-methyltetrahydrofuran, give colors reminiscent of those observed for the corresponding oxiranes under these conditions.[8,45a] The visible absorption spectra are essentially identical with those of the corresponding oxiranes with absorption maxima shifted by 1–5 nm. Such absorption maxima have been shown to exhibit a bathochromic shift with increasing irradiation times and hence it remains to be established how real these differences are.[45b] Thus caution must be exercised in attributing the photochromic behavior to the sulfites rather than to traces of oxirane generated under the low-temperature photolysis conditions. Direct spectroscopic comparison of the absorption intensity of the colored species obtained by these independent routes in rigid matrices is difficult since color development is not uniform and is restricted to the window surfaces. Thus absolute measurement of extinction coefficients is not feasible under these conditions. However, from a qualitative standpoint color development occurs more slowly in the case of the sulfites, which require longer irradiation times than needed for the corresponding oxiranes. Furthermore the color intensity is significantly lower for the former. Such differences would in fact be anticipated if initial oxirane formation is occurring and it is these species, produced in low concentration, which are actually responsible for the observed color. Although oxirane formation is not a detectable process at ambient temperatures (*vide supra*), it is conceivable that the [5 → 2 + 2 + 1] reaction of cyclic sulfites could occur in a concerted fashion at ambient temperatures without formation of the oxirane, and that the mechanistic process may be altered by sufficient cooling (−196°) so that discrete intermediates are stabilized. Under these conditions oxiranes may be implicated. The oxirane photochromism is believed to arise as a result of formation of oxoylides such as **45** formed by cleavage of the C–C bond[4,45] as shown in eq 16.



45 (16)

Huisgen and coworkers[46] have shown that in fact similar ylides when produced thermally from oxiranes may be trapped by dipolarophiles. These ylides may then fragment further in a thermal step or more likely by absorption of another photon to the carbene or alternatively recyclize reversibly to the oxirane. A detailed discussion of the probable reaction mechanism is given elsewhere.[4,8]

If the colored species obtained in the low-temperature irradiation of the sulfites are not identical with those obtained from the oxiranes, *i.e.*, if the 1–5 nm shift is a reflection of real differences in the structures, then perhaps ylides such as **46** may be formed by cleavage of the C–C bond as shown in eq 17 and then fragment further to give the carbene. This mode of opening seems unlikely in the absence of strain inherent in the corresponding oxiranes, but if such is the



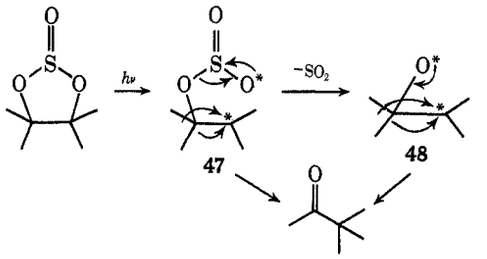
(17)

(45) (a) T. Do-Minh, A. M. Trozzolo, and G. W. Griffin, *J. Amer. Chem. Soc.*, **92**, 1402 (1970); (b) N. R. Bertoniere, Ph.D. Dissertation, Louisiana State University in New Orleans, 1971.

(46) H. Hamberger and R. Huisgen, *Chem. Commun.*, 1190 (1971); A. Dahmen, H. Hamberger, R. Huisgen, and V. Markowski, *ibid.*, 1192 (1971).

case alternate mechanistic pathways must be advanced to explain the occurrence of rearrangement products, *i.e.*, aryl migration as well as [5 → 3 + 2] cycloelimination to an alkene and sulfur trioxide.

The formation of rearrangement products is most economically rationalized on the basis of a mechanism involving a concerted Ar_1-3 migration after initial homolysis of the sulfite C–O bond to give **47**, although prior loss of sulfur dioxide and rearrangement *via* the intermediate **48** is not excluded (eq 18).



(18)

The intermediate **47** also may be invoked to explain the [5 → 3 + 2] cycloelimination reaction of sulfites to give sulfur trioxide, although a totally concerted elimination is certainly possible.

In summary, it is evident from this study that all of the cyclic sulfites examined with the exception of fluorenopinacol sulfite (**13**) are useful carbene precursors. It is also noteworthy that in all cases investigated excluding **13**, 1,2-aryl migration with loss of sulfur dioxide to give rearrangement products competes with carbene formation as does alkene formation with extrusion of sulfur trioxide.

From the considerations described above it appears that no single mechanism can satisfactorily explain the photochemical behavior of the sulfites and we believe that more than one process may be involved in the photofragmentation process. Further work is in progress to clarify these results.

Experimental Section

General.—All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer 337 and 257 spectrophotometers. The ultraviolet spectra were determined on Perkin-Elmer 202 and 450 spectrophotometers and the molar extinction coefficients were obtained on a Cary Model 15 spectrophotometer. The proton magnetic resonance spectra were determined on a Varian A-60 spectrophotometer using deuteriochloroform as the solvent with 1% tetramethylsilane as the internal standard unless otherwise specified. The mass spectral studies were conducted using a Hitachi Perkin-Elmer RMU-6E spectrometer.

Analytical gas chromatograms were obtained on a Perkin-Elmer Model 900 gas chromatograph equipped with a flame ionization detector using Perkin-Elmer support coated open-tubular (SCOT) capillary columns. Integration of peak areas was achieved either by multiplication of peak height by peak width at half height or by using a Hewlett-Packard Model 3370A electronic digital integrator. Preparative gas chromatographic separations were carried out on an Aerograph Model A-90P gas chromatograph using 0.25-in. columns. Silica gel G (PF_{254}, Brinkman Company) was used for thin and thick layer chromatographic separations.

Irradiations were conducted in serum capped 15 cm × 12.5 mm i.d. fused quartz tubes in a Rayonet photochemical reactor (The Southern New England Ultraviolet Co., Middletown, Conn.) using 16 8-W low pressure lamps unless otherwise specified. The lamps were either G8T5 (254 nm) or F8T5 (broad emission at 350 nm). A Rayonet MGR-100 Merry-Go-Round apparatus (The Southern New England Ultraviolet Co., Middletown, Conn.) was utilized in all kinetic studies to ensure uniform exposure of individual samples, which were rotated at 5 rpm. The solutions to be irradiated were degassed either by nitrogen sparging for 25 min or by the multiple freeze–thaw cycle technique.

Preparation of Benzopinacol Sulfite (7a).—A solution containing 1.4 g (12 mmol) of thionyl chloride in 5 ml of methylene chloride was added dropwise with stirring to a solution of 3.6 g (10 mmol) of benzopinacol in 20 ml of methylene chloride and 5 ml of pyridine. The reaction mixture was stirred at room temperature for 5 hr and the excess thionyl chloride was then destroyed by addition of water. The resulting mixture was treated with three 15-ml portions of hydrochloric acid (5%), and the organic phase was separated, washed repeatedly with water, and dried over anhydrous potassium carbonate. The residue remaining after removal of solvent under reduced pressure (3.0 g, 38%) was chromatographed on silica gel using benzene as the eluting solvent. The colorless crystals which deposited were recrystallized from ethanol to give the pure benzopinacol sulfite: mp 137–138°; ir 945, 1040 and 1240 cm^{-1}; pmr (CCl_4) τ 2.9 (m, aromatic); uv $\lambda_{max}^{C_2H_5OH}$ 266 nm (log ϵ 2.98), 261 (3.01), 254 (2.95); mass spectrum *m/e* 348, 332, 232, 182, and 105.

Anal. Calcd for $C_{26}H_{20}O_3S$: C, 75.72; H, 4.85. Found: C, 75.89; H, 4.72.

Preparation of 9-Fluorenopinacol.—9-Fluorenopinacol was prepared according to the procedure of Risinger and Eddy[47] by addition of zinc dust and sodium hydroxide to a solution of fluorenone cooled in ethanol to −5°. Recrystallization of the product from dilute ethanol gave the desired diol, mp 190–191° (lit.[48] mp 190–192°).

Preparation of 9-Fluorenopinacol Sulfite (13).—A solution of 0.6 g (5.0 mmol) of thionyl chloride in 5 ml of methylene chloride was added slowly with stirring to 9-fluorenopinacol (0.9 g, 3.0 mmol) at 0° in 10 ml of methylene chloride and 2 ml of pyridine. The resulting reaction mixture was stirred for 3 hr at room temperature and the product was isolated in the manner described earlier for **7a**. The crude product was recrystallized from methylene chloride–ethanol using Norit to give colorless needles: yield 0.7 g (70%); mp 175–178° dec; ir (KBr) 935 and 1215 cm^{-1}; pmr τ 2.7 (aromatic); uv $\lambda_{max}^{C_2H_5OH}$ 288 nm (log ϵ 4.16), 278 (4.29), 269 (4.20), 239 (4.77), 232 (4.75); mass spectrum *m/e* 344, 328, 316, 180, and 64.

Anal. Calcd for $C_{26}H_{16}O_3S$: C, 76.37; H, 3.92. Found: C, 76.02; H, 3.78.

Preparation of *meso*-Hydrobenzoin.—*meso*-Hydrobenzoin was prepared by sodium borohydride reduction of benzil employing the procedure described by Fieser,[49] mp 136–137° (lit.[49] mp 136–137°).

Preparation of *meso*-Hydrobenzoin Sulfite (17).—The procedure of Thompson and coworkers[14] was employed for the preparation of **17**. The crude product was crystallized from ether to yield the same major product reported by these investigators: mp 130–131° (lit.[14] mp 130–131°); ir ($CHCl_3$) 975, 1040, and 1210 cm^{-1}; pmr ($CDCl_3$) τ 3.0 (m, 10, aromatic), 3.85 (s, 2 methine); uv $\lambda_{max}^{C_2H_5OH}$ 268 nm (log ϵ 2.36), 264 (2.6), 258 (2.67), 252 (2.6); mass spectrum *m/e* 196, 180, 154, 126, and 105 (lit.[50] *m/e* 196, 180, 154, 126, and 105).

Preparation of *dl*-Hydrobenzoin.—*dl*-Hydrobenzoin was prepared according to the procedure outlined by Jenevein,[51] mp 120–121° (lit.[51] mp 120–121°).

Preparation of *dl*-Hydrobenzoin Sulfite (18).—*dl*-Hydrobenzoin sulfite was prepared by the same procedure employed for the meso isomer **17**. The crude product was recrystallized from ether–hexane, giving 0.8 g of white needles: mp 85–86° (lit.[14] mp 84–86°); ir (CCl_4) 965 and 1227 cm^{-1}; pmr ($CDCl_3$) τ 2.72 (m, 10, aromatic), 4.4, 4.85 (d, 2, benzylic); uv $\lambda_{max}^{C_2H_5OH}$ 269 nm (log ϵ 2.46), 263 (2.67), 257 (2.7), 252 (2.57); mass spectrum *m/e* 196, 180, 154, 126, and 105 (lit.[50] *m/e* 196, 180, 154, 126, and 105).

Preparation of *meso*-α,α′-Dimethylhydrobenzoin.—The meso

(47) G. E. Risinger and C. W. Eddy, *Chem. Ind. (London)*, 570 (1963).

(48) M. Gomberg and W. E. Bachmann, *J. Amer. Chem. Soc.*, **49**, 236 (1927).

(49) L. F. Fieser, "Organic Experiments," D. C. Heath, Boston, Mass., 1964, p 216.

(50) J. G. Pritchard and P. T. Funke, *J. Heterocycl. Chem.*, **3**, 209 (1966); P. Brown and C. Djerassi, *Tetrahedron*, **24**, 2949 (1968).

(51) R. M. Jenevein, Ph.D. Dissertation, Louisiana State University in New Orleans, 1969.

diol was obtained by addition of an excess of methyllithium to benzil as described by Stocker and coworkers.[52] Recrystallization from benzene–heptane yielded the pure *meso*-α,α'-dimethylhydrobenzoin, mp 120–121° (lit.[52] mp 120–121°).

Preparation of *meso*-α,α'-Dimethylhydrobenzoin Sulfite (40).—Thionyl chloride (3.6 g, 30 mmol) in 10 ml of methylene chloride was added slowly with stirring to 5.0 g (20 mmol) of *meso*-α,α'-dimethylhydrobenzoin in 20 ml of methylene chloride and 5 ml of pyridine at room temperature. After completion of the addition the reaction mixture was stirred for 4 hr and the excess thionyl chloride was removed by distillation under reduced pressure. The residue was dissolved in methylene chloride and the resulting solution was washed first with copper sulfate solution (5%) and then repeatedly with water. The organic phase was then dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The concentrate was chromatographed on alumina to give a viscous oil (4 g, 68%) which solidified on standing for 2 weeks. Recrystallization from methylene chloride–hexane gave the pure sulfite: mp 89°; ir ($CHCl_3$) 900, 1040, and 1222 cm^{-1}; pmr (CCl_4) τ 3.03 (m, 10, aromatic), 7.96 (s, 3, methyl), 8.16 (s, 3, methyl); uv $\lambda_{max}^{C_2H_5OH}$ 264 nm (log ϵ 2.59), 258 (2.72), 252 (2.62); mass spectrum *m/e* 224, 209, 181, 168, 126, 105, 104, 91, and 77.

Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.66; H, 5.55. Found: C, 66.43; H, 5.36.

Preparation of *dl*-α,α'-Dimethylhydrobenzoin.—This diol was prepared by the addition of freshly distilled 2,3-butanedione to phenyllithium as described by Stocker and coworkers.[52] The diol, mp 124–125° (lit.[52] mp 124–125°), was purified by recrystallization from heptane.

Preparation of *dl*-α,α'-Dimethylhydrobenzoin Sulfite (41).—*dl*-α,α'-Dimethylhydrobenzoin sulfite was prepared by addition of thionyl chloride (3.6 g, 30 mmol) in methylene chloride (10 ml) to the pinacol (5 g, 20 mmol) in 15 ml of methylene chloride and 5 ml of pyridine. The reaction mixture was worked up in a manner similar to that used for the meso isomer **40**. In this case, however, it was necessary to store the residual oil in the refrigerator for 6 weeks before solidification occurred (3.8 g, 85%). Purification of *dl*-α,α'-dimethylhydrobenzoin sulfite was achieved by recrystallization from aqueous methanol: mp 47–48°; ir ($CHCl_3$) 1223, 1070, 915 cm^{-1}; pmr (CCl_4) τ 2.6 (m, 10, aromatic), 8.38 (s, 3, methyl), 8.7 (s, 3, methyl); uv $\lambda_{max}^{C_2H_5OH}$ 263 nm (log ϵ 2.59), 257 (2.68), 252 (2.56); mass spectrum *m/e* 224, 208, 181, 168, 126, 105, 104, 91, and 77.

Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.66; H, 5.55. Found: C, 66.79; H, 5.65.

Preparation of Benzhydryl Methyl Ether (9).—The procedure of Gillis[53] was utilized for methylation of benzhydrol. Benzhydrol (5.0 g, 25 mmol) was added to a stirred suspension of 2.0 g (50 mmol) of finely powdered sodium hydroxide in 25 ml of dimethyl sulfoxide. To the resulting mixture was added 5.3 g (37 mmol) of methyl iodide and the solution was stirred for 3 hr. After dilution with 50 ml of water the product was extracted with ether, the organic phase was washed with water and dried over anhydrous sodium sulfate, and the volatile solvents were removed. The residual oil was then purified by distillation under reduced pressure, bp 105–106° (4 mm) [lit.[54] bp 146–148° (12 mm)].

Preparation of Benzyl Methyl Ether (19).—Benzyl alcohol (3.1 g, 30 mmol) was methylated in a manner similar to that used for benzhydryl alcohol. The benzyl methyl ether was purified by distillation at atmospheric pressure, bp 169–170° (lit.[55] bp 170°).

Preparation of Benzylcyclohexane (21).—Benzylcyclohexane was prepared as described by Smith[56] by treatment of cyclohexanone with benzylmagnesium bromide to give the 1-benzylcyclohexanol, which was subsequently dehydrated with iodine in toluene and then hydrogenated using palladium on charcoal as a catalyst. Purification was achieved by distillation, bp 141° (26 mm) [lit.[57] bp 133° (19 mm)].

(52) J. H. Stocker, P. Sidisunthorn, B. M. Benjamin, and C. J. Collins, *J. Amer. Chem. Soc.*, **82**, 3913 (1960).

(53) R. G. Gillis, *Tetrahedron Lett.*, 1413 (1968).

(54) G. von Wittig and W. Happe, *Justus Liebigs Ann. Chem.*, **577**, 205 (1947).

(55) W. T. Olson, H. F. Hipsher, C. M. Buess, I. A. Goodman, I. Hart, J. H. Lamneck, Jr., and L. C. Gibbons, *J. Amer. Chem. Soc.*, **69**, 2451 (1947).

(56) R. L. Smith, Ph.D. Dissertation, Louisiana State University in New Orleans, 1971.

(57) H. A. Smith, D. M. Alderman, Jr., C. D. Shacklett, and C. M. Welch, *J. Amer. Chem. Soc.*, **71**, 3772 (1949).

Preparation of 2- and 3-Benzylpentane (26 and 27, Respectively).—To the Grignard reagent prepared from 10.2 g (60 mmol) of benzyl bromide and 1.45 g (0.06 g-atom) of magnesium turnings was added 5.0 g (58 mmol) of 2-pentanone to yield 7.2 g (65%) of 1-phenyl-2-methylpentanol. A mixture of the crude pentanol (4.8 g), 1.5 ml of hydriodic acid, and 1.5 g of red phosphorus was heated under reflux for 8 hr with occasional addition of hydriodic acid until an aliquot sample, after dilution with ether and treatment with aqueous sodium carbonate and sodium bisulfite, yielded a colorless solution (*i.e.*, no trace of free iodine). The reaction mixture was then diluted with water and extracted repeatedly with ether. The combined organic phases were washed with sodium carbonate solution (10%), sodium bisulfite (5%), and water and dried over anhydrous magnesium sulfate, and the volatile solvent was removed under reduced pressure. From the residual oil pure 2-benzylpentane was obtained by preparative glc using a 4 m × 6 mm Apiezon L on Chromosorb P column at 180°: pmr (CCl_4) τ 2.9 (s, 5, aromatic), 7.5 (d, 2, benzylic), 8.5–9.1 (m, 8, aliphatic), and 9.11 (d, 3, methyl); mass spectrum *m/e* 162 (molecular ion).

The same procedure with minor modifications was used for the preparation of 3-benzylpentane. The requisite 3-benzylpentane was purified by glc as before: pmr (CCl_4) τ 2.86 (m, 5, aromatic), 7.5 (d, 2, benzylic), 8.6 (q, 4, methylene), 9.12 (t, 6, methyl); mass spectrum *m/e* 162 (molecular ion).

1-Phenylhexane (**25**) was purchased from Aldrich Chemical Co., Inc., Milwaukee, Wis., and used without further purification.

Preparation of *syn*-, *anti*-, and *trans*-2,3-Dimethyl-1-phenylcyclopropane (28, 29, and 30, Respectively).—The authentic addition products derived from phenylcarbene (**6**) and *cis*-2-butene were prepared according to the method of Smith[58] by photolysis of *trans*-2,3-diphenyloxirane in *cis*-2-butene to give the syn and anti isomers. The trans isomer **30** was obtained in a similar manner from *trans*-2-butene: syn isomer, pmr (CCl_4) τ 2.8 (s, 5, aromatic), 9.05 (s, 6, methyl); anti isomer, pmr (CCl_4) τ 2.82 (m, 5, aromatic), 8.87 (s, 6, methyl); trans isomer, pmr (CCl_4) τ 2.92 (s, 5, aromatic), 9.22 (d, 6, methyl). The mass spectra of all three isomeric 2,3-dimethyl-1-phenylcyclopropanes exhibit the anticipated molecular ion at *m/e* 146.

Preparation of *o,o'*-Bitolil.—*o,o'*-Bitolil was prepared by oxidation of 2,2'-dimethylbenzoin with copper sulfate and pyridine according to the method employed by Clarke and Dreger[42] for the synthesis of the parent compound benzoin. The 2,2'-dimethylbenzoin was obtained in turn by condensation of *o*-tolualdehyde as described by Adams and Marvel.[58] The crude *o,o'*-bitolil was recrystallized from ethanol, mp 92° (lit.[59] mp 92°).

Preparation of *meso*-2,2'-Dimethylhydrobenzoin.—The *o,o'*-bitolil (4.6 g, 20 mmol) was reduced with sodium borohydride in a manner similar to that employed by Fieser[49] for *meso*-hydrobenzoin. The crude product was recrystallized from aqueous ethanol: mp 104–105°; pmr ($CDCl_3$) τ 2.84 (m, 4, aromatic), 4.84 [s (broad), 1, benzylic], 7.7 [s (broad), 1, hydroxyl], and 7.84 (s, 3, methyl).

Preparation of *meso*-2,2'-Dimethylhydrobenzoin Sulfite (37).—The sulfite **37** was prepared from 2.4 g (10 mmol) of the corresponding pinacol and 1.3 g (12 mmol) of thionyl chloride as described for **18** (*vide supra*). The crude product (1.8 g, 70%) was recrystallized from methylene chloride–hexane to give pure 2,2'-dimethylhydrobenzoin sulfite: mp 152–153°; ir (KBr) 1220, 930, 960, 740, and 770 cm^{-1}; pmr ($CDCl_3$) τ 2.9 (m, 8, aromatic), 3.54 (s, 2, benzylic), and 7.88 (s, 6, methyl); uv $\lambda_{max}^{C_2H_5OH}$ 273 nm (log ϵ 2.83), 266 (2.89), 260 (2.79); mass spectrum *m/e* 224, 208, 168, 140, 120, 119, 92, and 91.

Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.66; H, 5.55. Found: C, 66.81; H, 5.63.

Preparation of *p,p'*-Bitolil (34).—*p,p'*-Bitolil (**34**) was obtained by oxidation of 4,4'-dimethylbenzoin (**33**) with copper sulfate and pyridine.[42] The corresponding 4,4'-dimethylbenzoin was prepared by utilizing the benzoin condensation with *p*-tolualdehyde.[58] Purification was achieved by recrystallization from ethanol, mp 102–103° (lit.[60] mp 102–103°).

Preparation of *meso*-4,4'-Dimethylhydrobenzoin (35).—4,4'-

(58) R. Adams and C. S. Marvel, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1964, p 94.

(59) M. S. Kharasch, W. Nudenberg, and S. Archer, *J. Amer. Chem. Soc.*, **65**, 495 (1943).

(60) M. Gomberg and W. E. Bachmann, *J. Amer. Chem. Soc.*, **50**, 2762 (1928).

Dimethylhydrobenzoin was prepared by sodium borohydride reduction of *p,p'*-bitolil: mp 144.5–145.5° (lit.[61] mp 145–146°); pmr ($CDCl_3$) τ 2.84 (s, 4, aromatic), 5.25 (s, 1, benzilic), 7.67 (s, 3, methyl), 7.9 [s (broad), 1, hydroxyl].

Preparation of *meso*-4,4'-Dimethylhydrobenzoin Sulfite (36).—The sulfite **36** was prepared in the usual manner from 2.4 g (10 mmol) of the diol **35** and 1.3 g (12 mmol) of thionyl chloride. The crude product was recrystallized from pentane to give the pure **36** (1.5 g, 50%): mp 82–83°; ir (KBr) 1220, 960, 840, and 780 cm^{-1}; pmr ($CDCl_3$) τ 3.1 (m, 8, aromatic), 3.95 (s, 2, methine), and 7.84 (s, 6, methyl); uv $\lambda_{max}^{C_2H_5OH}$ 273 nm (log ϵ 2.51), 268 (2.61), 263 (2.76), and 257 (2.68); mass spectrum *m/e* 224, 208, 168, 140, 120, 119, 92, and 91.

Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.66; H, 5.55. Found: C, 66.81; H, 5.76.

Preparation of *o*-Tolylcyclohexylmethane.—A solution of *o*-tolylcyclohexylmethanol (2.0 g, 10 mmol), prepared from cyclohexylmagnesium bromide and *o*-tolualdehyde, was heated under reflux with red phosphorus and hydriodic acid. The resulting crude *o*-tolylcyclohexylmethane was chromatographed over alumina after work-up in the manner previously described for **21** and the desired hydrocarbon was obtained as a colorless oil of sufficient purity for use: pmr (CCl_4) τ 3.1 (s, 4, aromatic), 7.6 (d, 2, benzylic), 7.7 (s, 3, methyl), and 8.7 (m, 11, cyclohexyl); mass spectrum *m/e* 188 (molecular ion).

Preparation of *p*-Tolylcyclohexylmethane (38).—A preparative procedure analogous to that described for the *o*-tolyl derivative was followed with the exception that *p*-tolualdehyde was used as the aldehyde substrate. The pure hydrocarbon was obtained as a colorless oil by preparative glc: pmr (CCl_4) τ 3.1 (s, 4, aromatic), 7.6 (d, 2, benzylic, J = 6 cps), 7.7 (s, 3, methyl), and 8.7 (m, 11, cyclohexyl); mass spectrum *m/e* 188 (molecular ion).

Preparation of Di-*o*-tolylmethane.—In a typical experiment 1.2 g (10 mmol) of *o*-tolualdehyde was added to the Grignard reagent prepared from 1.7 g (10 mmol) of *o*-bromotoluene and 0.26 g (0.01 g-atom) of magnesium and the reaction mixture was stirred for 12 hr at room temperature. The resulting mixture was hydrolyzed with dilute hydrochloric acid and extracted repeatedly with ether. The combined organic phases were washed with aqueous sodium carbonate and water, and finally dried over anhydrous sodium sulfate. The volatile solvents were then removed under reduced pressure and the resulting crude alcohol was crystallized from dilute ethanol to give the desired di-*o*-tolylcarbinol: mp 119–120° (lit.[62] mp 119–120°); yield 1.2 g (55%); pmr ($CDCl_3$) τ 2.7 (s, 8, aromatic), 3.88 (s, 1, benzylic), 7.74 (s, 6, methyl), and 8.00 [s (broad), 1, hydroxyl]. The alcohol (1.0 g, 5.0 mmol) prepared as described above was then heated under reflux with red phosphorus and hydriodic acid and the product was isolated and purified by chromatography on alumina: pmr (CCl_4) τ 3.0 (m, 8, aromatic), 6.18 (s, 2, benzylic), and 7.18 (s, 6, methyl); mass spectrum *m/e* 196 (molecular ion).

Preparation of Di-*p*-tolylmethane (39).—A preparative procedure similar to that employed for the analogous ortho-substituted hydrocarbon was used for the synthesis of di-*p*-tolylmethane from *p*-tolualdehyde and *p*-bromotoluene: mp 28° (lit.[63] mp 28.5°); pmr (CCl_4) τ 2.89 (s, 8, aromatic), 6.13 (s, 2, benzylic), and 7.74 (s, 3, methyl); mass spectrum *m/e* 196 (molecular ion).

Photolysis of Benzopinacol Sulfite (7a) in Methanol.—A solution of 0.10 g (2.5×10^{-4} mol) of benzopinacol sulfite (**7a**) dissolved in 10 ml of methanol was degassed utilizing the multiple freeze–thaw technique and irradiated for 12 hr in a quartz test tube.[64a] An absorption band at 1350 cm^{-1} characteristic of sulfur dioxide was observed in the infrared spectrum of an aliquot of the irradiated sample. The excess methanol was removed from the photolysis solution under reduced pressure and the components of the residual solid were separated by tlc (benzene–carbon tetrachloride, 65:35) into three fractions. The first fraction (12%) after recrystallization from ethanol (mp 235–236°) was found to be indistinguishable from 9,10-diphenylphenanthrene (**10**). An authentic sample of **10** was prepared by irradiation (254 nm) of tetraphenylethylene in methanol. The second fraction (40%) was shown to be benzhydryl methyl ether (**9**), spectroscopically identical with an authentic sample. The final fraction (15%) was identified as benzophenone by infrared spectroscopy. Under the conditions described no residual sulfite **7a** or tetraphenyloxirane (**12**) could be detected by tlc.

Relative Rates of Formation of Diphenylcarbene from Benzopinacol Sulfite (7a) and Tetraphenyloxirane (12).—In two identical quartz tubes were placed 3.0×10^{-2} mmol of benzopinacol sulfite (12.4 mg) and tetraphenyloxirane (10.44 mg) and each was dissolved in 10-ml aliquots of methanol containing 1.0×10^{-5} mol (1.6 mg) of phenylcyclohexane (Eastman Kodak Co., Rochester, N. Y.), which was employed as the internal standard. The tubes were sealed with rubber septa, degassed by nitrogen sparging, and irradiated[64b,d] for a total of 25 min. Aliquot samples (3 ml) were withdrawn after 4 and 13 min. The samples were analyzed by glc using a DC 550 SCOT 50-ft capillary column, temperature programmed from 110 to 140° at 5° per min. Enrichment techniques with authentic samples of benzhydryl methyl ether (**9**) and phenylcyclohexane (internal standard) permitted ready identification of the respective peaks in the chromatogram. Multiple runs of each sample were made and peak areas due to **9** and internal standard were determined by digital electronic integration. Their ratios were compared and absolute yields obtained from glc response factors were determined independently utilizing known solutions of **9** and phenylcyclohexane.

Irradiation of *meso*-Hydrobenzoin Sulfite (17) in Cyclohexane.—A solution of 0.065 g (0.25 mmol) of hydrobenzoin sulfite (**17**) in 10 ml of cyclohexane was irradiated for 15 hr.[64a] Analysis of the gaseous products by infrared and mass spectroscopy confirmed that sulfur dioxide is produced. The reaction mixture was concentrated under reduced pressure, and the residue was then separated preparatively into three main components by glc (Apiezon L, 0.25 in. × 12 ft column, 200°). The first component to emerge was found to be benzaldehyde, identical with an authentic sample. The second component was benzylcyclohexane (**21**), indistinguishable from an authentic sample. Diphenylmethane (**20**), having spectral characteristics identical with those of an authentic sample, was also separated. Examination of the reaction mixture by tlc confirmed that neither *trans*- nor *cis*-2,3-diphenyloxirane (**22** nor **23**) is produced in significant amounts.

Insertion Reactions of Phenylcarbene Generated from Diverse Sources in *n*-Pentane.—In each of four identical fused quartz tubes was placed 5.0×10^{-2} mmol of the carbene precursors to be compared. The specific amounts were 13.0 mg of *meso*-hydrobenzoin sulfite (**17**), 13 mg of *dl*-hydrobenzoin sulfite (**18**), 9.8 mg of *trans*-2,3-diphenyloxirane (**23**), and 5.9 mg of phenyldiazomethane (**24**). A 10-ml aliquot of a 1.0×10^{-5} *M* solution of amylbenzene (Aldrich Chemical Co., Inc., Milwaukee, Wis.) in 99% pure *n*-pentane (Columbia Organic Chemical Co., Inc., Columbia, S. C.) was transferred to each tube by means of a 10-ml pipette. The tubes were sealed with serum caps, degassed by nitrogen sparging using syringe needles, and irradiated[64b,d] for 25 min. A duplicate sample of phenyldiazomethane (**24**) was irradiated[64c,d] for 4 hr at 350 nm. The samples were then concentrated under reduced pressure and analyzed by glc. Satisfactory (base line) resolution of the benzyl pentanes **25**, **26**, and **27** was obtained using a DC 550 SCOT 50-ft capillary column which was temperature programmed from 75 to 145° at 1°/min from the time of injection of each individual run. Enrichment techniques employing authentic samples of the benzyl pentanes **25**, **26**, and **27** and the internal standard amylbenzene were used to establish the identity of these peaks in the resulting gas chromatograms. Multiple runs (4–6) were made for each sample and the requisite peak areas were determined by multiplying peak height by peak width at half peak height. In this manner areas of peaks corresponding to amylbenzene, **25**, **26**, and **27** were determined and the isomer ratios were then computed and tabulated for the individual carbene precursors (Table I). Absolute yields were obtained by determination of response factors utilizing standard solutions prepared from amylbenzene and authentic samples of the insertion products. Analysis by tlc (in benzene–carbon tetrachloride, 4:1) confirmed that no significant geometric isomerization of either the oxirane **23** or the sulfites **17** and **18** occurs under the reaction conditions and no detectable *cis*- or *trans*-diphenyloxirane (**22** or **23**) is formed in conjunction with the photocycloelimination reactions of the sulfite substrates.

(61) J. Grimshaw and J. S. Ramsey, *J. Chem. Soc. C*, 653 (1966).

(62) H. H. Hatt, *J. Chem. Soc.*, 1623 (1929).

(63) T. Reichstein and R. Oppenauer, *Helv. Chim. Acta*, **16**, 1373 (1933).

(64) Irradiations were conducted in serum-capped quartz or Pyrex tubes as specified using a Rayonet RPR 100 photochemical reactor (The Southern New England Ultraviolet Co., Middletown, Conn.) equipped with (a) 16 8-W low-pressure G8T5 lamps (254 nm); (b) eight 8-W low-pressure G8T5 lamps (254 nm); (c) 16 8-W low-pressure F8T5 lamps (350 nm) as a light source; (d) a Rayonet MGR 100 Merry-Go-Round apparatus (The Southern New England Ultraviolet Co., Middletown, Conn.) rotated at 5 rpm was utilized in all rate studies to ensure uniform exposure of individual samples.

Addition of Phenylcarbene Generated from Diverse Sources to *cis*-2-Butene. Stereospecificity of Cycloaddition.—Irradiations in this study were conducted in 150 × 24 mm i.d. fused quartz tubes which had been modified to accept an Aerosol Compatibility Head Assembly equipped with a valve (Fischer and Porter Co., Warminister, Pa.) (alternatively a Griffin–Worden Quartz Pressure Vessel[9]). The substrate to be photolyzed was placed in the quartz tube, the Aerosol Compatibility Head was secured, and the system was evacuated (~0.5 mm). The assembly was then immersed in a Dry Ice–acetone bath and sufficient *cis*-2-butene (99.91 mol %, Phillips Petroleum Co., Bartesville, Okla.) was admitted by means of a tygon tube to obtain approximately 5.0×10^{-3} *M* solutions. The specific weights of the compounds employed in the study were 13.0 mg (5.0×10^{-5} mol) of *meso*-hydrobenzoin sulfite (**17**), 13.0 mg (5.0×10^{-5} mol) of *dl*-hydrobenzoin sulfite (**18**), and 15.4 mg (7.88×10^{-5} mol) of *trans*-2,3-diphenyloxirane (**23**). The resulting solutions were degassed by the multiple freeze–thaw technique and irradiated[64b,d] for 9 min. Upon completion of the irradiations the excess *cis*-2-butene was collected by distillation into a cold trap.

Subsequent analysis of the *cis*-2-butene confirms that no geometric isomerization of this substrate takes place under the reaction conditions. A 1-ml aliquot of a standard (0.54 mg/ml, 3.34×10^{-6} mol) solution of phenylhexane (Matheson Coleman and Bell Co., East Rutherford, N. J.) in methylene chloride was added to each solution and the reaction mixture was then analyzed by glc. The isomeric cyclopropanes were resolved using two DC 550 SCOT 50-ft capillary columns in series and a program in which the temperature is varied from 100 to 130° at 0.5°/min. Enrichment techniques employing authentic samples of each of the isomeric 2,3-dimethyl-1-phenylcyclopropanes **28**, **29**, and **30** and phenylhexane, the internal standard, were used to confirm the identity of the peaks in the resulting gas chromatograms. Multiple runs (4–6) of each sample were made and the area of each peak was determined by multiplication of the peak height by the peak width at half height. The desired isomer ratios were calculated and compared for each of the phenylcarbene precursors. No concomitant geometric isomerization of the substrates occurs as indicated by tlc analysis.

Irradiation of Sulfites in Methanol at 350 nm.—Individual solutions (2.5×10^{-4} mol) of **7a**, **17**, **18**, **40**, and **41** in 10 ml of methanol contained in Pyrex tubes were degassed by nitrogen sparging and irradiated[64c] for 24 hr at 350 nm. After removal of the solvent under reduced pressure in each case the sulfites were recovered quantitatively and no methyl ether formation could be detected by tlc.

Irradiation of 9-Fluorenopinacol Sulfite (13) in 2,3-Dimethyl-2-butene at 350 nm.—A solution of 0.10 g (0.25 mmol) of 9-fluorenopinacol sulfite (**13**) in 10 g (0.13 mol) of 2,3-dimethyl-2-butene was irradiated[64c] for 5 hr after degassing by the multiple freeze–thaw technique. The solvent was removed from the resulting yellow solution by distillation and the residue upon recrystallization from methylene chloride–hexane gave colorless prisms, mp 260°, found to be indistinguishable from the 9-diphenylene-10-phenanthrone (**19**).[7,19] No evidence (tlc) was obtained for the formation of 2,2,3,3-tetramethylspiro[cyclopropane-1,9′-fluorene] (**14**).

Irradiation of *meso*- and *dl*-α,α′-Dimethylhydrobenzoin Sulfite (40 and 41, Respectively) in Methanol.—Solutions of 0.15 g (5.0×10^{-5} mol) of the *meso*- and *dl*-α,α′-dimethylhydrobenzoin sulfite (**40** and **41**) in 15 ml of methanol were photolyzed[64a] for 8 hr at 254 nm in a quartz tube after degassing by nitrogen sparging. After completion of the irradiation the effluent gas was analyzed by infrared and mass spectrometry and found to contain sulfur dioxide. The solutions were then concentrated under reduced pressure and the residue was separated into four fractions by tlc (benzene). The fourth fastest moving band was extracted and was found to be α-phenethylmethyl ether indistinguishable spectroscopically (ir, pmr) from an authentic sample. The third band on elution with chloroform yielded a colorless solid which crystallized from absolute ethanol to give colorless needles, mp 143–144° (12 mg, 12%), found to be indistinguishable from 9,10-dimethylphenanthrene (**44**). The remaining slowest moving fractions were found to contain primarily acetophenone and starting material. The presence of acetophenone was confirmed by enrichment techniques using glc analysis on a DC 550 SCOT 50-ft capillary column operated isothermally at 100°.

Irradiation of *meso*-4,4′- and *meso*-2,2′-Dimethylhydrobenzoin Sulfite (36 and 37, Respectively) in Cyclohexane at 254 nm.—Solutions of 0.10 g (3.5×10^{-4} mol) of the sulfites **36** and **37** in 25 ml of cyclohexane were degassed by the multiple freeze–thaw technique and irradiated[64a] in a quartz vessel at 254 nm for 8 hr. The solutions were then concentrated under reduced pressure and the residue was analyzed by glc using a DC 550 SCOT 50-ft capillary column operated at 130°. Compounds identified among the photoproducts of **36** by the enhancement technique utilizing authentic samples included *p*-tolualdehyde, *p*-tolylcyclohexylmethane (**38**), and di-*p*-tolylmethane (**39**), while *o*-tolualdehyde, *o*-tolylcyclohexylmethane, and di-*o*-tolylmethane were observed among the photolysis products of **37**. The analysis was conducted under conditions which would have permitted recognition of the di-*o*-tolylmethane from di-*p*-tolylmethane.

Irradiation of Deoxybenzoin (31) and Diphenylacetaldehyde (32).—Solutions of 0.2 g (1.2 mmol) of diphenylacetaldehyde and deoxybenzoin in 25 ml of cyclohexane were degassed by nitrogen sparging and irradiated[64b] at 254 nm for 8 hr. The solutions were then concentrated under reduced pressure and the residue was subjected to pmr analysis in carbon tetrachloride. Interpretation of pmr spectral data indicated that 70% of the diphenylacetaldehyde had been decarbonylated to diphenylmethane, while no diphenylmethane was observed in the photolysis of deoxybenzoin.

Thermolyses of Sulfites.—The thermolyses were carried out in boiling (a) xylene (140°), (b) decane (168°), and (c) hexadecane (275°). The solvent in each case was removed by distillation under reduced pressure and the residue was examined for products. Benzopinacol sulfite (**7a**) after 6 hr at 140° was converted cleanly into tetraphenyloxirane (**12**), mp 205–206° (from MeOH), indistinguishable from an authentic sample. After 6 hr at 140°, 9-fluorenopinacol sulfite (**13**) gave colorless prisms (from benzene), mp 260–261°, found to be identical with the spiro ketone 9-diphenylene-10-phenanthrone (**16**) obtained by photolysis of the sulfite **13**. The hydrobenzoin sulfites (**17** and **18**) were found to be stable at 140 and 168° (8 hr). At 275° (6 hr) the *dl* sulfite **18** was found to give mainly diphenylacetaldehyde while meso sulfite **17** gave no detectable quantities of this aldehyde (glc). The dimethylhydrobenzoin sulfites **40** and **41** were also found to be stable at 140° (12 hr).

Registry No.—**7a**, 34737-62-7; **10**, 602-15-3; **13**, 34737-64-9; **17**, 19455-94-8; **18**, 10359-60-1; **36**, 34737-67-2; **37**, 34712-68-0; **40**, 34737-68-3; **41**, 34737-69-4; **44**, 604-83-1; *meso*-2,2′-dimethylhydrobenzoin, 34737-70-7.

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