CH=CHCHCl, $J_{12} = 5.4$, $J_{23} = 14.4$ Hz); **21**, 1.60 (d, 3, $CH_3$, $J_{45} = 6.8$ Hz), 4.00 (m, 2, $CH_2$), 4.42 (m, 1, CHCl), 5.74 (m, 2, CH=CH).

Summary of ir data ($cm^{-1}$, $CCl_4$): **19a,** 983 and 930 (CH=$CH_2$), 3090, 2980, 2920, 1445, 1360, 1200, 750, 650 $cm^{-1}$; **20a,** 720, ($CS_2$, cis CH=CH), 1665 (C=C), 3040, 2950, 2910, 2860, 1430, 1380, 1310, 1270, 1200, 1170, 960, 920, 680; **20b,** 956 (trans CH=CH), 1670 (C=C), 3040, 2970, 2950, 2910, 2890, 2860, 1425, 1370, 1195, 1170, 670; **21,** 957 (trans CH=CH), 1670 (C=C), 3040, 2970, 2910, 2860, 1440, 1380, 1250, 1215, 1010, 685, 645.

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**Registry No.**—**1,** 542-92-7; **2,** 592-57-4; **3a,** 6108-61-8; **3b,** 5194-51-4; **3c,** 5194-50-3; **4a,** 1574-41-0; **4b,** 2004-70-8; **5,** 51502-28-4; **6,** 31572-43-7; **7,** 31572-45-9; **8,** 31572-44-8; **9,** 53921-00-9; **10,** 53920-98-2; **11,** 54112-34-4; **12,** 53920-99-3; **13,** 57256-15-2; **14,** 57256-16-3; **15,** 57256-17-4; **16,** 57273-83-3; **17,** 57256-18-5; **18,** 57256-19-6; **19a,** 57256-20-9; **19b,** 53920-93-7; **20a,** 53920-95-9; **20b,** 53920-94-8; **21,** 53920-96-0.

## References and Notes

(1) (a) V. L. Heasley, G. E. Heasley, S. K. Taylor, and C. L. Frye, *J. Org. Chem.,* **35,** 2967 (1970); (b) G. E. Heasley, V. L. Heasley, S. L. Manatt, H. A. Day, R. V. Hodges, P. A. Kroon, D. A. Redfield, T. L. Rold, and D. E. Williamson, *ibid.,* **38,** 4109 (1973).

(2) Previous studies on the chlorination of conjugated dienes follow. Butadiene: (a) M. L. Poutsma, *J. Org. Chem.,* **31,** 4167 (1966); (b) V. L. Heasley, G. E. Heasley, R. A. Loghry, and M. R. McConnell, *ibid.,* **37,** 2228 (1972). Isoprene: (c) G. D. Jones, N. B. Tefertiller, C. F. Raley, and J. R. Runyon, *ibid.,* **33,** 2946 (1968). Cyclopentadiene: (d) V. L. Heasley, G. E. Heasley, P. D. Davis, D. M. Ingle, and K. D. Rold, *ibid.,* **39,** 736 (1974). *trans,trans*-2,4-Hexadiene: (e) M. S. Edmondson, *Diss. Abstr.,* 3914 (1971).

(3) For a discussion of competition between radical and ionic mechanisms in chlorination of alkenes, see (a) M. L. Poutsma, *J. Am. Chem. Soc.,* **87,** 2172 (1965); (b) *J. Org. Chem.,* **31,** 4167 (1966).

(4) The attack by chloride ion in **22d** is anti to the chlorine atom already bonded to carbon but the dichlorides formed (both 1,2 and 1,4) from **22d** are the same as those resulting from direct syn addition of both chlorine atoms to the same side of the diene, i.e., they are syn products. For previous discussions of this matter see ref 1b and studies on the bromination of the 1-phenylpropenes [J. H. Rolston and K. Yates, *J. Am. Chem. Soc.,* **91,** 1469 (1969); R. C. Fahey and H. J. Schneider, *ibid.,* **90,** 4429 (1968)].

(5) Although there is evidence (mainly under conditions other than those employed in electrophilic addition) that bromine is a better bridging atom than chlorine [see, e.g., F. Freeman, *Chem. Rev.,* **75,** 454 (1975)], the ability of chlorine to form stable bridged ions in electrophilic addition has been amply demonstrated. Stereospecific anti addition has been observed with a diversity of alkenes such as cyclopentene,[2d] *cis*-2-butene,[3a] and *cis*-di-*tert*-butylethylene: R. C. Fahey, *J. Am. Chem. Soc.,* **88,** 4681 (1966).

(6) For a further discussion see our recent paper on the addition of bromine chloride to **1**: V. L. Heasley, C. N. Griffith, and G. E. Heasley, *J. Org. Chem.,* **40,** 1358 (1975).

(7) Edmondson[2e] reports that essentially equal amounts of anti and syn 1,2-dichloride are obtained from chlorination of **3b** in several solvents. Since our syn:anti 1,4-dichloride ratios and 1,4:1,2 ratios are in good agreement with his, the discrepancy on the ratio of 1,2-dichlorides may be due to the fact that his mixtures of erythro and threo dichlorides were analyzed via diimide reduction to the 2,3-dichlorohexanes. We were able to achieve direct VPC separation of the 1,2-dichlorides and also observed that the NMR spectra of the mixture of 1,2-dichlorides confirmed our VPC analysis.

(8) This trend has been observed for chlorination and bromination of butadiene in several solvents [V. L. Heasley, G. E. Heasley, R. A. Loghry, and M. R. McConnell, *J. Org. Chem.,* **37,** 2228 (1972)]. Chlorination of isoprene[2c] gives more 1,4 than 1,2 addition in most solvents; bromination of isoprene also occurs predominantly 1,4 [V. L. Heasley, C. L. Frye, R. T. Gore, and P. S. Wilday, *ibid.,* **33,** 2342 (1968)].

(9) We assume that attack on a bridged bromonium ion (covalently bonded to both carbon atoms) is essentially a nucleophilic displacement and that opening by attack on the double bond would be an example of the SN2′ mechanism. Although a syn stereochemistry is generally accepted for SN2′, the evidence for this has been questioned [F. G. Bordwell, *Acc. Chem. Res.,* **3,** 281 (1970)]. Liotta [C. L. Liotta, *Tetrahedron Lett.,* 523 (1975)] and Fukui [K. Fukui, *ibid.,* 2427 (1965)] have predicted on theoretical grounds that SN2′ attack should be syn to the leaving group.

(10) The relatively low yields of dichlorides obtained with some of the dienes (particularly with **2**) is probably due to competing substitution reactions. De La Mare and Wong [*Recl. Trav. Chim. Pays-Bas,* **87,** 824 (1968)] have investigated the ionic chlorine substitution reaction which occurs with **4a,b.** We observed that chlorination of **2** in carbon tetrachloride produced benzene (identified by the NMR singlet at $\delta$ 7.26) in a mole ratio equal to the dichlorocyclohexenes. Benzene would be obtained by HCl elimination from the allylic substitution product of cyclohexadiene (**2**), 5-chloro-1,3-cyclohexadiene (benzene hydrochloride).

(11) J. W. Hamersma and E. I. Snyder, *J. Org. Chem.,* **30,** 3985 (1965).

(12) M. L. Poutsma, *J. Am. Chem. Soc.,* **87,** 2162 (1965).

(13) N. Isaacs and D. Kirkpatrick, *Tetrahedron Lett.,* 3869 (1972).

(14) Edmondson[2e] proved the structure of the principal 1,4-dichloride of **3b** (**15**) by diimide reduction to *dl*-2,5-dichlorohexane.

(15) G. E. Heasley, R. V. Hodges, and V. L. Heasley, *J. Org. Chem.,* **39,** 1769 (1974).

(16) C. Moureu, M. Murat, and L. Tampier, *Bull. Soc. Chim. Fr.,* **29,** 29 (1921).

(17) Since the major crotonaldehyde dichloride isomer is the same from chlorination of crotonaldehyde and when derived from the chlorination product of **3b** (in $CCl_4$), the major dichloride from **3b, 18,** can be assigned the erythro structure on the assumption that chlorine addition to the largely *trans*-crotonaldehyde would be predominantly anti. The chlorination product (in $CCl_4$) from **3a** yielded a crotonaldehyde dichloride mixture in which the major dichloride was the opposite to that obtained from **3b,** so it follows that the major dichloride (**14**) of **3a** ($CCl_4$) is threo. Additional evidence for assignment of erythro and threo structures was obtained by converting the chlorination product of **4a** to crotonaldehyde dichlorides. The crotonaldehyde dichloride obtained in major amount (>95%) had a VPC retention time identical with that of the major crotonaldehyde dichloride derived from **3a.** Thus the assignment of the threo structure to **14** follows if the nearly stereospecific addition to the 3,4 bond in **4a** (and **4b**) is assumed to be anti.

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

G. W. Griffin,* R. L. Smith,[3] and A. Manmade

*Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70122*

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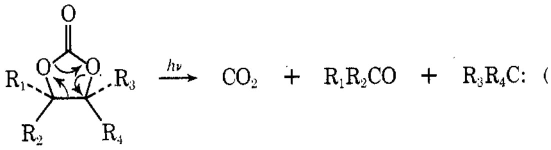
Cyclic arylpinacol carbonates undergo photoinduced [5 → 2 + 2 + 1] cycloeliminations to give arylcarbenes. The carbonates studied include benzopinacol carbonate, *meso*- and *dl*-hydrobenzoin carbonates, and the *dl*- and *meso*-$\alpha,\alpha'$-dimethylhydrobenzoin carbonates. Arylcarbenes formed by photolysis of these substrates react in methanol to give methyl ethers and the properties of phenylcarbene obtained from the *meso*- and *dl*-hydrobenzoin carbonates are found to be virtually identical with those obtained from conventional precursors such as *trans*-2,3-diphenyloxiranes and phenyldiazomethane; i.e., the secondary to primary insertion selectivity in pentane and the stereospecificity in the addition to *cis*-2-butene are the same.

It has become increasingly apparent that both thermal and photocycloelimination reactions, like the reverse reactions of cycloaddition, have broad synthetic utility.[4,5,6] We have recently described the [5 → 2 + 2 + 1] photocycloelimination of pinacol sulfites[4] and as part of our continuing research program in this area have investigated the chemical response of a series of cyclic pinacol carbonates of the type 1 to ultraviolet radiation. It has previously been established that a variety of polyaryl substituted heterocyclic substrates undergo photocycloelimination reactions to give arylcarbenes.[5] In view of our experience with related sulfites[4] and phospholanes[7] which photolyze to arylcarbenes it appeared probable that carbonates of the type 1 also would undergo facile photocycloelimination in a [5 → 2 + 2 + 1] manner to give carbenes (eq 1).[8–10]



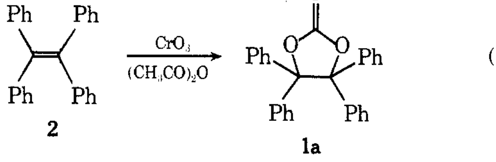
(1)

1a, $R_1 = R_2 = R_3 = R_4 = Ph$
b, $R_1 = R_3 = Ph; R_2 = R_4 = H$
c, $R_1 = R_4 = Ph; R_2 = R_3 = H$
d, $R_1 = R_3 = Ph; R_2 = R_4 = CH_3$
e, $R_1 = R_4 = Ph; R_2 = R_3 = CH_3$

## Results and Discussion

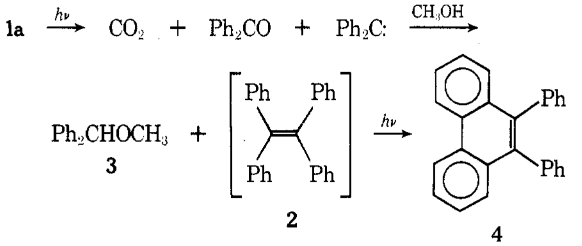
Benzopinacol carbonate (**1a**), a cyclic carbonate incorporating structural features designed to facilitate photocycloelimination, was selected as a substrate for preliminary photocycloelimination studies. The anticipated carbene, diphenylmethylene, has been studied extensively both chemically[11a] and spectroscopically by optical[12] and EPR[13] techniques. Kirmse, Hörner, and Hoffmann[11a] have established that diphenylcarbene obtained photolytically from diphenyldiazomethane reacts with alcohols to give ethers. They proposed that the carbene is nucleophilic in character and is readily protonated in alcohols to give the benzhydryl carbonium ion which subsequently solvolyzes to benzhydryl ethers; however, this mechanism has been challenged recently.[11b] Diphenylcarbene, a triplet ground state species, reacts with alkanes and alkenes by hydrogen abstraction to give benzhydryl radicals which subsequently dimerize or react in other ways.[5b] These free-radical processes complicate investigations involving addition and insertion reactions of this divalent species and consequently methanol was selected as the most convenient solvent trapping agent for screening potential carbonate precursors for arylcarbene formation.

Two general methods for the preparation of cyclic carbonates, namely treatment of the requisite 1,2-diol with phosgene[14] or diethyl carbonate,[15] failed to give **1a** when applied to benzopinacol. The desired benzopinacol carbonate (**1a**) was finally obtained, albeit in low yield (17%), by oxidation of tetraphenylethylene (**2**) with chromium trioxide in acetic anhydride (eq 2). This method is described by Mosher and co-workers,[16] who allude to the difficulties encountered in preparing **1a** from the diol by conventional methods.



(2)

Photolysis (254 nm) of benzopinacol carbonate (**1a**) in methanol induces a [5 → 2 + 2 + 1] cycloelimination reaction of the type anticipated to give diphenylcarbene as evidenced by formation of benzhydryl methyl ether (**3**, 60%) (eq 3).[2a]

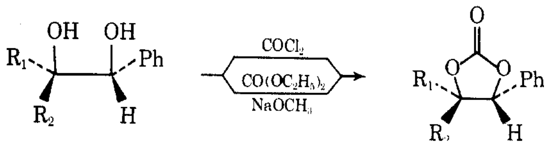


(3)

Other compounds identified among the photolysis products of **1a** include benzophenone (15%) and 9,10-diphenylphenanthrene (**4**, 10%). It was shown independently that tetraphenylethylene (**2**) undergoes dehydrophotocyclization under the reaction conditions and thus **4** is probably a secondary photoproduct arising from **2** as indicated in eq 3.[17] Similar results were obtained upon photolysis of benzopinacol sulfite and it was concluded that the alkene **2** in that case was formed as a result of a [5 → 3 + 2] cycloelimination reaction involving extrusion of sulfur trioxide.[4] A concerted [5 → 3 + 2] cycloelimination reaction leading to **2** is more difficult to formulate in the case of the carbonate **1a** and the origin of the tetraphenylethylene (**2**) remains to be established in this case; however, diphenylcarbene dimerization is an improbable reaction at ambient temperature in fluid solutions and is excluded as a significant source of **2**.[18] The presence of carbon dioxide among the photoproducts of **1a** was confirmed by means of mass spectrometry.

A sequential mechanism involving initial formation of tetraphenyloxirane (**5**) might be invoked to explain the photolysis of **1a** and would appear to be a reasonable proposal in light of the previously reported thermolytic conversions of carbonates to oxiranes[19,20] and the known photolability of the latter, which are excellent carbene precursors.[10] No tetraphenyloxirane (**5**) could be detected by TLC among the photoproducts obtained from **1a** in methanol even under conditions where conversion levels were minimal (10–15%). It is clear from calculations based upon the relative extinction coefficients and comparative fragmentation rates that shielding of the oxirane **5** by **1a** should be efficient enough to ensure buildup of detectable levels of **5**. For this reason a concerted cycloelimination mechanism is preferred for **1a** although a stepwise homolytic or ionic fragmentation process which circumvents formation of the oxirane **5** cannot be excluded at this time. Benzopinacol carbonate, like tetraphenyloxirane (**5**) and benzopinacol sulfite, proved photostable when irradiated in a Pyrex vessel at a longer wavelength (350 nm).

In order to evaluate the generality of the carbonate cycloelimination reaction the photochemistry of *meso*- and *dl*-hydrobenzoin carbonates (**1b** and **1c**, respectively) was also studied. The synthesis of the phenylcarbene precursors **1b** and **1c** (48 and 54%, respectively) was realized by treatment of *meso*- and *dl*-hydrobenzoin (**6b** and **6c**, respectively), with either phosgene or diethyl carbonate[14,15] (eq 4).



(4)

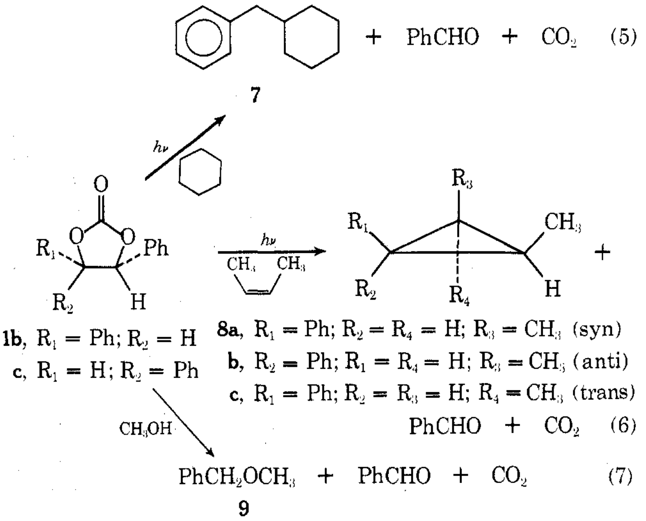
6b, $R_1 = Ph; R_2 = H$
c, $R_1 = H; R_2 = Ph$

1b, $R_1 = Ph; R_2 = H$
c, $R_1 = H; R_2 = Ph$

Phenylcarbene, the anticipated transient from **1b** and **1c**, has previously been characterized extensively and the ground state, like that of diphenylcarbene, has been designated as triplet on the basis of EPR and optical emission studies.[10,13] The EPR spectrum, which should be very sensitive to the geometry of phenylcarbene, has been shown to be independent of the structure of the precursor in several cases including the diazo compound, a geminal diazide, and benzaldehyde *p*-toluenesulfonylhydrazone in a variety of environments indicating that the observed structure is an intrinsic property of the carbene.[21,22] The emission spectrum of phenylcarbene also has been observed in a hydrocarbon matrix at −196°.[10] Extended Hückel calculations by Hoffmann and co-workers[23] are also interpreted as supporting a ground state triplet structure for phenylcarbene.

Extensive effort has been devoted to characterization of the reactive state(s) of phenylcarbene. The chemical behavior of phenylcarbene generated photochemically from phenyldiazomethane,[24–26] phenyloxiranes and cyclopropanes,[27] and cyclic pinacol sulfites[2,4] appears to be that of a singlet and is independent of precursor in both C–H insertion and alkene addition reactions. It has been found that the stereospecificity of cyclopropanation is reduced and an increase in alkene formation occurs when the photolysis is conducted in frozen *cis*-2-butene matrices (−196°). Triplet phenylcarbene in rapid thermal equilibrium or formed by decay from the singlet has been advanced as the key intermediate in the low-temperature matrix experiments; i.e., the degree of stereospecificity of cyclopropanation decreases with a concomitant increase in abstraction recombination processes leading to alkenes as triplet phenylcarbene chemistry intervenes.[26a] Comparative studies of 2-*n*-butylphenylcarbene generated by triplet photosensitized and thermal decomposition of the corresponding diazo compound have also been conducted and no significant difference in behavior was discerned between the carbenes generated from the two sources.[25c] To explain this observation it was proposed that singlet and triplet phenylcarbene equilibrate with each other more rapidly than they undergo C–H insertion or C=C addition reactions. In fact there appears to be a growing conviction that a facile equilibrium exists between triplet and singlet phenylcarbene.[26b]

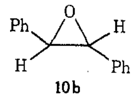
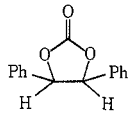
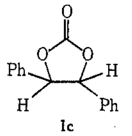
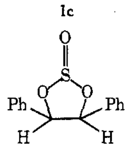
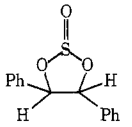
Upon photolysis (254 nm) both *meso*- and *dl*-hydrobenzoin carbonates (**1b** and **1c**, respectively) give a species which exhibits the reactions anticipated for phenylcarbene, namely, insertion into saturated carbon–hydrogen bonds such as those of cyclohexane to give benzylcyclohexane (**7**) (eq 5),[25] addition to *cis*-2-butene to give the syn and anti cyclopropanes **8a** and **8b**, respectively (eq 6),[24,28] and reaction with methanol to yield benzyl methyl ether (**9**) (eq 7).[11] Other products resulting from the fragmentation of **1b** and **1c** include benzaldehyde and carbon dioxide. The substrates **1b** and **1c** like **1a** were found to be photostable when irradiated with a lower energy source (>300 nm) in a Pyrex vessel and complete recovery of the starting material was achieved in both cases.



**1b**, $R_1 = Ph; R_2 = H$
**c**, $R_1 = H; R_2 = Ph$

**8a**, $R_1 = Ph; R_2 = R_4 = H; R_3 = CH_3$ (syn)
**b**, $R_2 = Ph; R_1 = R_4 = H; R_3 = CH_3$ (anti)
**c**, $R_1 = Ph; R_2 = R_3 = H; R_4 = CH_3$ (trans)

Table I
Insertion Selectivity of Phenylcarbene Generated from Diverse Sources

| Phenylcarbene precursor | Yield, % (25 min, 8 lamps) 254 nm | Insertion ratio (11 + 12)/13 | Insertion ratio[a] 11/12 |
|---|---|---|---|
|  **10b** | 45.4 | 8.33 ± 0.14[b] | 1.35 ± 0.04 |
|  **1b** | 3.8 | 8.47 ± 0.20 | 1.42 ± 0.03 |
|  **1c** | 5.2 | 8.27 ± 0.23 | 1.42 ± 0.03 |
|  **14** | 5.5 | 8.48 ± 0.24 | 1.41 ± 0.05 |
|  **15** | 6.6 | 8.00 ± 0.18 | 1.45 ± 0.02 |
| $PhCHN_2$ | 18.3[c] | 8.38 ± 0.19 | 1.33 ± 0.09 |

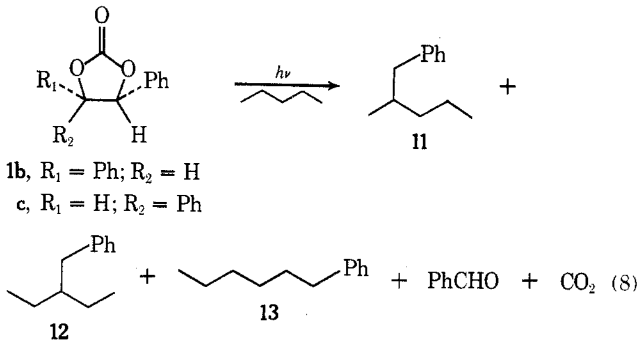
[a] Statistically corrected for the number of hydrogen atoms of each type. [b] Limits of error in each case represent standard deviations obtained by multiple integration of several chromatograms. [c] 350 nm, 16 lamps, 4 hr.

While irradiation (254 nm) of **1b** or **1c** in cyclohexane affords benzylcyclohexane (**7**) as well as benzaldehyde and carbon dioxide, it is significant that under the conditions employed for the photolysis no detectable amounts of the corresponding oxiranes, i.e., *cis*-2,3-diphenyloxirane (**10a**) and/or *trans*-2,3-diphenyloxirane (**10b**) in the case of **1b** and **1c**, were observed by TLC or $^1H$ NMR techniques. Competitive rate studies of the photofragmentation of **1c** and *trans*-2,3-diphenyloxirane (**10b**) in cyclohexane confirm that the initial oxirane cycloelimination rate exceeds that of **1c**. The faster rate observed for oxirane photolysis may be attributed in large measure to the differences in strain and extinction coefficients for the two substrates at 254 nm; however, the latter is not sufficiently great to allow **10b**, if formed as an intermediate, to escape detection.

Although it is apparent from the chemical data that both **1b** and **1c** undergo [5 → 2 + 2 + 1] cycloelimination reactions to produce "free" carbene, the characteristic phenylcarbene EPR signal could not be observed upon photolysis of these substrates for reasons yet undetermined.[29] Similar results were observed for *trans*-2,3-diphenyloxirane (**10b**) and triphenyloxirane where no EPR signal was detected for phenylcarbene despite convincing chemical evidence for its formation.[27] In the absence of direct EPR and/or optical spectroscopic data, it was necessary to obtain further chemical proof for the contention that **1b** and **1c** are indeed phenylcarbene precursors.

Competitive insertion experiments prove particularly useful as a method for comparing divalent carbon species generated from different sources such as **1b** and **1c**. Gutsche and co-workers[25] have previously determined the insertion selectivity of phenylcarbene generated from the conventional precursor phenyldiazomethane. Additional data on the selectivity of this carbene formed from a variety of other precursors including the oxirane **10b** have been reported by Griffin and co-workers.[4,27] A similar study of the insertion selectivity of the species generated from the carbonates **1b** and **1c** was initiated in connection with present work.

Solutions of the carbonates **1b** and **1c** of equal concentration were made in *n*-pentane and photolyzed (254 nm) simultaneously under identical conditions using the "merry-go-round" technique to ensure uniform exposure. Insertion product ratios and absolute yields were determined gas chromatographically employing an internal standard and predetermined response factors. 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 the required level.



**1b**, $R_1 = Ph; R_2 = H$
**c**, $R_1 = H; R_2 = Ph$

**11**

**12**

**13**

The results of the insertion studies conducted with the carbonates **1b** and **1c** are tabulated for comparison along with the corresponding data for the oxirane **10b**, the sulfites **14** and **15**, and phenyldiazomethane. In a typical experiment the three insertion products **11**, **12**, and **13** were obtained from *dl*-hydrobenzoin carbonate (**1c**) in the ratio of 6.12:2.16:1.00, respectively. The ratio of the combined amounts of 2- and 3-benzylpentanes **11** and **12**, respectively (formed by insertion into the six secondary C–H bonds) to 1-phenylhexane (**13**) (produced by attack at the six primary C–H bonds) was established as 8.27 ± 0.23 (see Table I). The ratio of 2- to 3-benzylpentane correspondingly is 2.84, which when statistically corrected gives a selectivity factor between secondary hydrogens of $C_2H$ or $C_4H$ over $C_3H$ of 1.42.

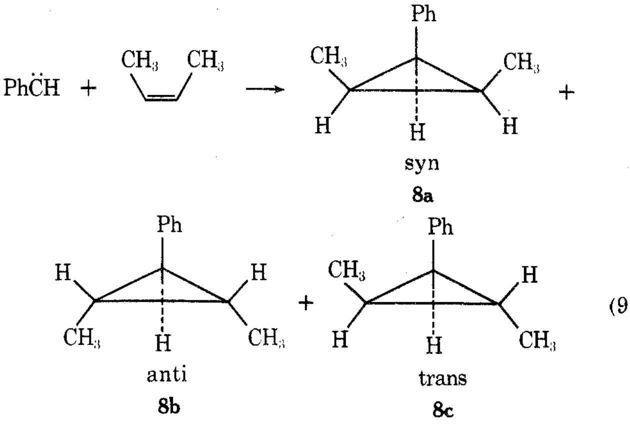
The results obtained in all cases substantiate the original proposal that the photolysis of cyclic carbonates does in fact give rise to species virtually indistinguishable chemically from those produced from conventional carbene precursors such as *trans*-2,3-diphenyloxirane (**10b**) and phenyldiazomethane. Higher yields are obtained with the oxirane **10b** and the diazo precursor (Table I), which indicates that their rate of fragmentation exceeds that of **1b** and **1c**. It remains to be determined if the quantum yield is higher for the former pair or if the difference in rate in only a reflection of their higher extinction coefficients. The carbonates presently under examination do afford significantly higher yields of insertion products upon prolonged irradiation and are of preparative value; however, determination of meaningful selectivity factors was, of course, of paramount importance in the present study, and photolyses were conducted at conversion levels only sufficient to permit reliable analyses to be conducted.

The stereochemistry of the cyclic carbonate precursors **1b** and **1c** exerts little or no influence upon the observed insertion selectivity factors, although the initial fragmentation rates for the *dl* isomer **1c** may be slightly higher. This is not unexpected in view of the higher extinction coefficient observed for this diastereomer at 254 nm.

Similar behavior was observed for the corresponding cyclic sulfites **14** and **15**. Analysis at low conversions (10%) where shielding of the alternate isomer if formed should be relatively effective shows that within the limits of detectability ($^1H$ NMR and TLC) interconversion of the two diastereomers **1b** and **1c** does not occur. Furthermore, no fragmentation was observed when the carbonates **1b** and **1c** were irradiated in *n*-pentane at 350 nm for extended periods.

Whether a concerted or stepwise mechanism, perhaps involving the oxiranes, is operative remains to be established, although a stepwise mechanism circumventing the oxiranes is presently favored since neither *cis*- nor *trans*-2,3-diphenyloxirane (**10a** and **10b**, respectively) could be detected by TLC among the reaction products of either **1b** or **1c**.

Quantitative evaluation of the selectivity exhibited by phenylcarbene in the possible modes of addition to *cis*-2-butene has been widely employed as a sensitive method of comparing the properties of this species generated from different sources and for assessing the extent of triplet participation.[24,25,30] In order to complement our insertion studies we have conducted similar addition experiments with *cis*-2-butene using the cyclic carbonate precursors **1b** and **1c**. Solutions of known concentrations of **1b**, **1c**, and **10b** were irradiated in *cis*-2-butene at 254 nm. The photolysis mixtures were analyzed by GLC as described above for **11**, **12**, and **13**, and the isomeric cyclopropanes **8a–c** were identified by comparison of retention times with authentic samples obtained by preparative scale photolyses utilizing *trans*-2,3-diphenyloxirane (**10b**) as the phenylcarbene source. The identities of the resulting isomeric cyclopropanes obtained from photolyses in *cis*- and *trans*-2-butene and separated by preparative GLC were readily established by comparison of $^1H$ NMR chemical shifts of the methyl protons which had previously been reported.[24] The addition studies using *cis*-2-butene were conducted using shorter irradiation times (9 min) than those employed in the C–H insertion reactions in order to preclude photoisomerization of the photolabile cyclopropanes and preserve product ratios which would in fact reflect the rates of the primary addition processes.[31,32,33] The reactions are highly stereospecific (>95%) in each case and from the results of the comparative studies delineated in Table II, it is clear

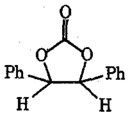
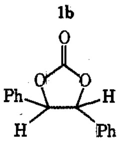
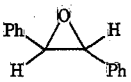


syn
**8a**

anti
**8b**

trans
**8c**

Table II
Stereoselectivity of Addition of Phenylcarbene from Diverse Sources to 2-Butene

| Phenylcarbene precursor | Syn/anti ratio |
|---|---|
|  1b | 1.18 ± 0.01[a] |
|  1c | 1.19 ± 0.01 |
|  10b | 1.19 ± 0.01 |

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

that the stereochemistry of addition (syn/anti ratio) is essentially invariant regardless of source and agree with the results previously reported by Closs and Moss.[24]

The cycloaddition results coupled with the comparative C–H insertion data (vide supra) leave little doubt that a common intermediate is involved which we believe is "free" phenylcarbene on the basis of the insensitivity of chemical behavior on precursor structure. It is assumed that phenylcarbene is formed in the singlet state and adds to *cis*-2-butene faster than decay to the triplet ground state can occur. It appears, however, that a small amount of competitive intersystem crossing to triplet phenylcarbene must occur, since 2–5% of *trans*-2,3-dimethyl-1-phenylcyclopropane (**8c**) is produced in all cases studied. It is believed that this is a primary product of addition and not the result of isomerization since the major primary products, cyclopropanes **8a** and **8b**, were found to be stable to the reaction conditions provided that the irradiation times are not extended beyond the time employed (9 min).

While explanations may be advanced to account for the observed independence of C–H insertion and addition selectivity on the origin of the carbene, insufficient data are available to provide a definitive mechanistic interpretation for this behavior. It has been established in other systems (i.e., geminal diazide, diazo, and oxirane precursors) that there is sufficient freedom for carbene precursor geometries differing by 10° to yield the same final geometry,[21] although the proposition that the strained oxirane **10b** and the diazo precursor should give isoenergetic nascent carbene appears unreasonable to us. Equally unlikely we feel is the proposal that the insertion and addition reactions are insensitive to energetic factors, although it may be argued that thermal equilibration to a common vibrational level of the same state occurs prior to insertion or addition. Certainly if equilibration of the singlet and triplet states of phenylcarbene occurs more rapidly than insertion and addition, as has been proposed,[25c] then the product distribution would not reflect the properties of the nascent carbene.

A study of the photolability of the acetophenone pinacol carbonates **1d** and **1e** has also been conducted and on the basis of preliminary photolysis experiments (254 nm) it is clear that both the meso and *dl* isomers (**1d** and **1e**, respectively), like the corresponding sulfites,[4] undergo [5 → 2 + 2 + 1] photocycloelimination to give methylphenylcarbene.[34] The requisite *meso*- and *dl*-$\alpha,\alpha'$-dimethylhydrobenzoin carbonates (**16** and **17**, respectively) were prepared by treatment of the corresponding hydrobenzoins with diethyl carbonate[15] and phosgene,[14] respectively. Irradiation of **1d** or **1e** in methanol affords $\alpha$-phenethyl methyl ether (20%) and acetophenone identified by GLC analysis using enrichment techniques with authentic samples. Additional evidence that the photolysis of **1d** and **1e** affords methylphenylcarbene was obtained by photolysis (254 nm) of these carbonates in cyclohexane, whereupon $\alpha$-methylbenzylcyclohexane is produced. A more detailed comparative study of the photochemistry of **1d** and **1e** as well as the corresponding sulfites and isomeric 2,3-diphenyl-2,3-dimethyloxiranes, which are all methylphenylcarbene precursors, is in progress.

## Experimental Section

**Apparatus.** Irradiation were conducted in serum-capped 15 cm × 12.6 mm i.d. fused quartz tubes (unless otherwise specified) in an air-cooled Rayonet RPR-100 chamber reactor (The Southern New England Ultraviolet Co., Middletown, Conn.) utilizing the stated number of G8T5 (254 nm) or F8T5/BLB (350 nm) 8-W low-pressure lamps at a temperature of approximately 40°. All samples were degassed by nitrogen sparging for at least 10 min prior to irradiation. A Rayonet MGR-100 merry-go-round apparatus (The Southern New England Ultraviolet Co., Middletown, Conn.) was employed in all kinetic studies to ensure uniform radiation of the individual samples which were rotated at 5 rpm during the course of photolysis. The quartz tubes used in all kinetic investigations were fabricated from a single length of 12.6 mm i.d. fused quartz tubing to ensure that the vessels used in any given run had identical properties. Several additional precautions were taken in all kinetic investigations; the solutions involved were thermally equilibrated to 25° in a water bath, and the ultraviolet lamps and chamber reactor were allowed to stabilize for a 10-min period prior to sample insertion.

Analytical gas chromatograms were obtained on either Perkin-Elmer Model 810 or Model 900 gas chromatographs equipped with flame ionization detectors. Support-coated open tubular (SCOT) capillary columns proved particularly effective in the isomer separation problems encountered in this study. Absolute yields were obtained by determination of the gas chromatographic response factors utilizing authentic mixtures of known concentration of an internal standard (phenylcyclohexane or *n*-amylbenzene) and authentic samples of the reaction products. All lamp emission spectra were determined on an Aminco-Bowman spectrophotofluorimeter.

The proton magnetic resonance spectra were determined on a Varian A-60 $^1$H NMR spectrometer with 1% tetramethylsilane as an internal standard. A Hitachi Perkin-Elmer RMU-6E mass spectrometer was used for all mass spectral analyses. Ultraviolet absorption spectra were recorded on a Cary Model 15 spectrophotometer in rectangular cells of 1 cm path length with flat optical quartz or Suprasil windows. All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Silica gel G ($PF_{254}$) on glass plates was used for thin and thick layer chromatographic separations. Resolution was confirmed by exposure of the chromatogram to short-wavelength ultraviolet light (Blak-Ray UVL-21) and/or developed in iodine vapor. Liquid–liquid partition chromatographic separations were obtained on a 164 cm × 42 mm i.d. glass column utilizing Celatom Filter Aid as the solid support; the column eluents were monitored on a Perkin-Elmer Model 202 ultraviolet–visible spectrometer and fractions were collected with an automatic fraction collector.

**Preparation of Benzopinacol Carbonate (1a).** The method used for the preparation of **1a** is a modification of that employed by Mosher, Steffgen, and Lansbury.[16] A solution of 95 ml of acetic acid and 75 ml of acetic anhydride which contained a 2.00-g (6.05 mmol) sample of tetraphenylethylene was treated with 1.21 g (12.0 mmol) of chromium trioxide in the presence of 5.86 g (60 mmol) of potassium acetate. The crude product mixture deposited upon addition of 200 ml of water, and the compounds were separated by thick layer chromatography using a solvent system of 4:1 benzene–carbon tetrachloride. The carbonate was collected on a filter and recrystallized from aqueous ethanol to give 410 mg (17%) of benzopinacol carbonate (**1a**), mp 170–171° (lit.[16] mp 170–171°).

**Preparation of Tetraphenyloxirane (5).** To a stirred solution of 4.00 g (1.21 × $10^{-2}$ mol) of tetraphenylethylene in 140 ml of chloroform was added 2.67 g ($1.32 \times 10^{-2}$ mol) of solid *m*-chloroperbenzoic acid (85%) while the temperature was maintained at 20° with a water bath. The resulting mixture was stirred at room temperature overnight, and the disappearance of tetraphenylethylene was monitored by TLC utilizing an eluent mixture of benzene–carbon tetrachloride (4:1). Upon completion of the reaction, the excess peracid was destroyed by slow addition of sufficient 10% aqueous sodium sulfite solution to render the solution neutral to starch–iodide paper. The mixture was then transferred to a separatory funnel and washed repeatedly with 10% aqueous sodium bicarbonate solution. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The resulting residue was recrystallized from methanol and 2.61 g (62%) of tetraphenyloxirane (5), mp 204–205° (lit.[35a] mp 204–205°, 208–210° [35b]) was obtained.

**Preparation of Benzhydryl Methyl Ether (3).** The desired ether 3 was prepared from benzhydrol by a modification of the method outlined by Gillis[36] and the procedures are described in detail elsewhere.[4] Purification of 3 was achieved by distillation under reduced pressure, bp 105–106° (4 mm) [lit.[37] 146–148° (12 mm)].

**Relative Rates of Formation of Diphenylcarbene from Benzopinacol Carbonate (1a) and Tetraphenyloxirane (5).** In each of two identical clear fused quartz tubes was placed $2.47 \times 10^{-2}$ mmol of the compound to be irradiated [9.70 mg of benzopinacol carbonate (1a) or 8.61 mg of tetraphenyloxirane (5)]. A 10-ml aliquot of anhydrous methanol containing $2.18 \times 10^{-3}$ g ($1.36 \times 10^{-5}$ mol) of phenylcyclohexane was added to each tube by means of a 10-ml volumetric pipet. The tubes were sealed, degassed by nitrogen sparging, equilibrated at 25° in a water bath, and irradiated for a total of 14 min using eight G8T5 low-pressure mercury lamps. Aliquots (3 ml) of the solutions under study were withdrawn by syringe during the photolysis after total exposure times of 4 and 9 min. The resulting solutions were concentrated under reduced pressure and analyzed by GLC utilizing an Apiezon L SCOT 50 ft capillary column (The Perkin-Elmer Corp., Norwalk, Conn.) operated isothermally at 200°. Enrichment techniques employing authentic samples of benzhydryl methyl ether (3) and the internal standard (phenylcyclohexane) permitted identification of the peaks in the resulting gas chromatograms. Multiple runs of each sample were made, and the requisite peak areas were determined by multiplication of peak height by peak width at one-half peak height. The peak areas due to 3 and phenylcyclohexane were tabulated and their ratios compared. Absolute yields were obtained by determination of the GLC response factors using known solutions of phenylcyclohexane and 3. Subsequent TLC analysis (4:1 benzene–carbon tetrachloride) revealed that no detectable tetraphenyloxirane (5) was present in the carbonate photolysis mixture.

**Irradiation of Benzopinacol Carbonate (1a) in Methanol.** A 106-mg ($2.72 \times 10^{-4}$ mol) sample of benzopinacol carbonate (1a) was dissolved in 5 ml of methanol in a 15 cm × 24 mm i.d. clear fused quartz tube which had been modified to accept an aerosol compatibility head assembly[38] or alternatively a Griffin-Worden pressure vessel was employed.[39] The sample was then degassed using the freeze–thaw method prior to irradiation for 14 hr using 16 G8T5 low pressure mercury lamps. Upon completion of the photolysis, the gases evolved were examined mass spectrometrically, and found to contain a substantial amount of carbon dioxide. The mass spectrometer was calibrated against air prior to analysis of the effluent gases from the reaction mixture. The excess methanol was then removed under reduced pressure from the reaction mixture, and the resulting residue was separated by TLC utilizing an eluent mixture of 2:1 benzene–carbon tetrachloride. The following pure photolysis products were isolated, and are listed in order of decreasing $R_f$ values: 9,10-diphenylphenanthrene (4, 10%) [spectroscopically identical with authentic sample prepared by photolysis (254 nm) of tetraphenylethylene in methanol[17]], benzhydryl methyl ether (3, 60%), and benzophenone (15%), both identical with authentic samples. No residual carbonate 1a or tetraphenyloxirane could be detected by TLC [benzene–carbon tetrachloride (4:1)].

**Irradiation of Benzopinacol Carbonate (1a) in Methanol at 350 nm.** A 58-mg ($1.4 \times 10^{-4}$ mol) sample of benzopinacol carbonate (1a) was dissolved in 10 ml of methanol in a 15 cm × 1.8 cm i.d. Pyrex tube, and irradiated for 16 hr utilizing 16 F8T5/BLB low pressure mercury lamps (350 nm). Upon completion of the irradiation, the volatile solvent was removed under reduced pressure and subsequent analysis of the residue by infrared and TLC (4:1 benzene–carbon tetrachloride) confirmed that no detectable photoproducts were formed upon irradiation of 1a under these conditions.

**Preparation of *meso*-Hydrobenzoin (6b).** *meso*-Hydrobenzoin was prepared by sodium borohydride reduction of benzil as described by Fieser.[40] The crude product was recrystallized from aqueous ethanol, mp 136–137° (lit.[40] mp 136–137°).

**Preparation of *meso*-Hydrobenzoin Carbonate (1b).** A modification of the procedure employed by Ludwig and Piech[14] for the preparation of cyclic 1,3-diol carbonate esters was utilized. A solution of 500 mg (2.33 mmol) of *meso*-hydrobenzoin (6b) in pyridine was placed in a three-necked round-bottom flask, equipped with a gas dispersion tube, thermometer, and an exhaust outlet. Phosgene was introduced slowly into the stirred solution which had been previously cooled to 15° at a rate sufficient to maintain the reaction temperature at approximately 35°. After an excess of phosgene had been added to the mixture, the reaction vessel was protected with a drying tube and the resulting solution stirred for 6 hr at room temperature. The system was subsequently flushed with nitrogen and the solvent and excess phosgene subsequently removed under reduced pressure while exercising the usual precautions for disposing of phosgene. The resulting residue was taken up in methylene chloride and washed twice with water and once with a saturated cupric nitrate solution. The resulting organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Recrystallization of the residue from aqueous ethanol afforded 270 mg (48%) of pure *meso*-hydrobenzoin carbonate (1b), mp 126–127° (lit.[15] mp 127°).

**Preparation of *dl*-Hydrobenzoin (6c).** The compound was prepared by an adaptation of the method described by Berti and Bottari.[41] *trans*-2,3-Diphenyloxirane (10b) was treated with trifluoroacetic acid to give the monoester, which was then treated with ethanolic potassium hydroxide according to the procedure outlined by Jenevein.[42] Isolation of the crude product and subsequent recrystallization from heptane yielded the desired *dl*-glycol 6c, mp 120–121° (lit.[42] mp 120–121°).

**Preparation of *dl*-Hydrobenzoin Carbonate (1c).** An aliquot (4.0 g) of a solution of phosgene in benzene (12.5%) was added slowly with stirring to a solution containing 500 mg (2.30 mmol) of *dl*-hydrobenzoin (6c) and 460 mg (5.80 mmol) of pyridine in 25 ml of anhydrous benzene. The rate of addition was controlled to maintain the temperature of the reaction mixture between 30 and 35°. After addition was completed, the resulting mixture was stirred overnight and the crude carbonate 1c was isolated in a manner identical with that described for the meso isomer and recrystallized from aqueous ethanol to give 300 mg (54%) of *dl*-hydrobenzoin carbonate (1c), mp 110.0–110.5° (lit.[43] mp 110°).

**Preparation of *trans*-2,3-Diphenyloxirane (10b).** The procedure used was identical with that previously described for the preparation of tetraphenyloxirane (5). A 6.0-g (33 mmol) sample of *trans*-stilbene upon treatment with *m*-chloroperbenzoic acid afforded 4.12 g (63%) of *trans*-2,3-diphenyloxirane (10b), mp 69–70° (lit.[35b] mp 69–70°).

**Preparation of Phenyldiazomethane.** Phenylhydrazone was prepared by treatment of benzaldehyde with hydrazine hydrate and barium oxide according to the method outlined by Curtius and Pflug.[44] Yellow mercuric oxide was added to the phenylhydrazone in pentane as described by Staudinger and Gaule,[45] and the resulting suspension shaken for 3 hr. The mixture was then filtered, and the volatile solvents removed under reduced pressure to give the desired reddish-brown phenyldiazomethane, which was prepared freshly and used immediately in all experiments.

**Preparation of Benzyl Methyl Ether (9).** The ether 9 was prepared by an adaption of the method outlined by Gillis[36] and employed for benzhydryl methyl ether 3 and has been described previously.[4] Distillation at atomospheric pressure gave the pure benzyl methyl ether (9), bp 169–170° (lit.[46] bp 170°).

**Irradiation of *meso*- and *dl*-Hydrobenzoin Carbonates (1b and 1c, respectively) in Methanol at 254 nm.** The carbonates 1b and 1c were irradiated in methanol under conditions described for the photolysis of benzopinacol carbonate in methanol. The resulting products, benzyl methyl ether (9) and benzaldehyde, were identified by GLC using enrichment techniques.

**Irradiation of *meso*- and *dl*-Hydrobenzoin Carbonates (1b and 1c, Respectively) at 350 nm.** In two 15 cm × 18 mm i.d. Pyrex tubes were placed 50 mg ($2.1 \times 10^{-4}$ mol) samples of the *meso*- and *dl*-hydrobenzoin carbonates (1b and 1c respectively) in 10 ml of methanol. The solutions were irradiated using 16 F8T5/BLB mercury lamps (350 nm) for a period of 14 hr. Removal of the volatile solvent under reduced pressure and subsequent infrared and TLC [benzene–carbon tetrachloride (4:1)] analyses of the residue revealed that **1b** and **1c** are photostable under these conditions.

**Preparation of Benzylcyclohexane (7).** Benzylcyclohexane was prepared as described earlier[4] by treatment of cyclohexanone with benzylmagnesium bromide to give the 1-benzylcyclohexanol,[47] 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.[48] bp 132° (19 mm)].

**Relative Rates of Formation of Phenylcarbene from *dl*-Hydrobenzoin Carbonate (1b) and *trans*-2,3-Diphenyloxirane (10b) in Cyclohexane.** In each of two identical, clear fused quartz tubes was placed $4.07 \times 10^{-2}$ mmol of the compound under investigation [9.80 mg of *dl*-hydrobenzoin carbonate (**1b**), or 8.81 mg of *trans*-2,3-diphenyloxirane (**10b**)]. A 10-ml aliquot of cyclohexane containing 2.16 mg ($1.35 \times 10^{-2}$ mmol) of phenylcyclohexane was transferred to each tube by means of a 10-ml volumetric pipet. The tubes were degassed, sealed, and photolyzed using the "merry-go-round" technique for a total of 7 min utilizing four G8T5 8-W low-pressure mercury lamps. Irradiations were interrupted after total exposure times of 1 and 4 min, and 3-ml aliquot samples were withdrawn with a syringe as previously described. The samples were concentrated under reduced pressure, and analyzed by GLC using a single DC-550 SCOT 50 ft capillary column operated isothermally at 150°. Enrichment techniques employing authentic samples of benzylcyclohexane (**7**) and the internal standard (phenylcyclohexane) permitted confirmation of the identity of these peaks in the resulting gas chromatograms. Multiple runs of each sample were made, and the requisite peak areas were obtained by multiplying peak height by peak width at one-half peak height. The peak areas due to **7** and phenylcyclohexane were tabulated and their ratios compared. Enhancement studies with authentic samples also demonstrated the presence of benzaldehyde and bicyclohexyl among the photolysis products of both the oxirane **10b** and the carbonate **1b**. Subsequent TLC analysis [benzene–carbon tetrachloride (4:1)] revealed no photoisomerism of either **10b** or **1b** under the reaction conditions, and no detectable oxirane **10b** was found among the carbonate photoproducts.

**Preparation of 2- and 3-Benzylpentane (11 and 12, Respectively).** The synthesis of **11** and **12** was accomplished by techniques previously described in detail.[4] The requisite 1-phenylhexane (**13**) was purchased (Aldrich Chemical Co., Inc., Milwaukee, Wis.).

**Insertion of Phenylcarbene Generated from Other Sources in *n*-Pentane.** In each of four identical, fused quartz tubes was placed $3.30 \times 10^{-2}$ mmol of the substrate to be studied. The specific amounts employed were as follows: 7.94 mg of *meso*-hydrobenzoin carbonate (**1b**), 7.93 mg of *dl*-hydrobenzoin carbonate (**1c**), 6.48 mg of *trans*-2,3-diphenyloxirane (**10b**), and 3.90 mg of phenyldiazomethane. A 10-ml aliquot of a $1.0 \times 10^{-5}$ *M* solution of amylbenzene in *n*-pentane (99%) was transferred to each tube by means of a 10-ml volumetric pipet. The tubes were sealed, degassed by nitrogen sparging, equilibrated to 25° in a water bath, and irradiated for 25 min utilizing the "merry-go-round" technique with eight G8T5 low-pressure mercury lamps. A duplicate sample of phenyldiazomethane was irradiated for 4 hr utilizing 16 F8T5/BLB mercury lamps (350 nm). Upon completion of the irradiations, the samples were concentrated at room temperature under reduced pressure and analyzed by GLC. Satisfactory resolution of the resulting benzylpentanes, **11**, **12**, and **13**, was obtained using a DC-550 SCOT 50 ft capillary column and temperature programming from 75° to 145° at 2°/min. The programmed temperature rise was begun simultaneously with sample injection, and the final temperature was held for 2 min upon termination of each run. Enrichment methods using authentic samples of each of the benzylpentane isomers **11**, **12**, and **13** and the internal standard (amylbenzene) confirmed the identity of these peaks in the resulting gas chromatograms. Each sample was injected several times, and the resultant peak areas were obtained by multiplying peak height by peak width at one-half peak height. In this manner, the areas of the peaks corresponding to **11**, **12**, and **13** and amylbenzene were determined and tabulated. The ratios of the isomers were calculated and compared for each separate carbene precursor. Absolute yields were obtained by determination of the GLC response factors utilizing standard solutions of amylbenzene and authentic samples of the reaction products. Further enhancement studies demonstrated that benzaldehyde is also present in the photolysis mixtures obtained from the oxirane **10b**, and both the carbonates **1b** and **1c**. Subsequent TLC analysis employing an eluent mixture of benzene–carbon tetrachloride (4:1) revealed that no photoisomerism to give the alternate isomer occurs with either the oxirane **10b** or the isomeric carbonates **1b** and **1c**. Furthermore, neither *cis*- nor *trans*-2,3-diphenyloxirane (**10a** and **10b**, respectively) was detected as a photoproduct of photolysis.

**Preparation of *syn*-, *anti*-, and *trans*-2,3-Dimethyl-1-phenylcyclopropanes (8a, 8b, and 8c, Respectively).** Authentic samples of the cyclopropanes **8a** and **8b** were prepared from *cis*-2-butene and phenylcarbene generated photochemically from *trans*-2,3-diphenyloxirane (**10b**). A 2.00-g (0.01 mol) sample of *trans*-diphenyloxirane (**10b**) was dissolved in 20 ml of *cis*-2-butene (99.91 mol %) and placed in a 15 cm × 24 mm i.d. quartz tube which had been modified to accept an aerosol compatibility head.[38] Alternatively a Griffin-Worden quartz pressure vessel may be used.[39] The head was secured and the solution degassed by the multiple "freeze–thaw" method prior to irradiation for 24 hr employing 16 G8T5 low-pressure mercury lamps. The excess *cis*-2-butene was then removed by short-path distillation and the residue subjected to preparative GLC using a 12 ft × 0.25 in. 10% Dow Corning silicone high vacuum grease on Chromosorb P column operated isothermally at 150°. Judicious collection procedures yielded two of the pure cis isomers with the following $^1$H NMR spectral characteristics which agree with previously reported data:[24] syn [$^1$H NMR ($CCl_4$) $\tau$ 2.80 (s, 5, phenyl), 9.05 (s, 6, methyl)] and anti [$^1$H NMR ($CCl_4$) $\tau$ 2.92 (s, t, phenyl), 8.87 (s, 6, methyl)] (**8a** and **8b**, respectively). The mass spectra in both cases exhibited the expected molecular ion, *m/e* 146.

A sample of **8c** was obtained by a similar photolysis of *trans*-2,3-diphenyloxirane (**10b**) in *trans*-2-butene (99.63 mol %). Isolation procedures as outlined for **8a** and **8b** afforded the pure trans isomer **8c** [$^1$H NMR ($CCl_4$) $\tau$ 2.02 (s, 5, phenyl), 9.22 (d, 6, methyl)]. The mass spectrum of **8c** displayed the anticipated molecular ion, *m/e* 146.

**Addition of Phenylcarbene Generated from Diverse Sources to *cis*-2-Butene.** Irradiations were conducted in 150 × 24 mm i.d. fused quartz tubes which had been modified to accept an aerosol compatibility head assembly[38] or alternatively in a Griffin-Worden pressure vessel.[39] The substrate to be photolyzed was placed in the quartz pressure tube, and the head secured prior to evacuation of the system. The assembly was then immersed in a dry ice-acetone bath, and sufficient *cis*-2-butene (99.91 mol %) was admitted by means of a coupling tube to obtain a solution which was approximately $5.0 \times 10^{-3}$ *M*. The specific weights of the compounds employed follow: 15.32 mg ($7.88 \times 10^{-5}$ mol) of *trans*-2,3-diphenyloxirane (**10b**), 15.31 mg ($6.40 \times 10^{-5}$ mol) of *meso*-hydrobenzoin carbonate (**1b**), and 11.13 mg ($4.65 \times 10^{-5}$ mol) of *dl*-hydrobenzoin carbonate (**1c**). The solutions were degassed using the multiple "freeze–thaw" method, and irradiated for 9 min at 254 nm using eight G8T5 low-pressure mercury lamps. Upon completion of photolysis, the excess *cis*-2-butene was collected and subsequent GLC analysis revealed that no isomerization of this substrate had occurred under the reaction conditions. A 1-ml aliquot of a methylene chloride solution containing 0.543 mg ($3.34 \times 10^{-6}$ mol) of 1-phenylhexane was added to each reaction mixture by means of a 1-ml volumetric pipet. The reaction mixtures were then concentrated under reduced pressure and analyzed by GLC. Satisfactory resolution of the isomeric cyclopropanes formed during photolysis was acheived utilizing two DC-550 50 ft SCOT capillary columns in series, and temperature programming from 100 to 128° at 0.5°/min. The programmed temperature rise was begun simultaneously with sample injection. Sample enrichment techniques employing authentic samples of each of the isomeric 2,3-dimethyl-1-phenylcyclopropanes **8a**, **8b**, and **8c** and the internal standard (1-phenylhexane) allowed identification of these peaks in the resulting gas chromatograms. Multiple runs of each sample were made, and the resulting peaks were sufficiently symmetrical to permit the peak areas to be determined by multiplication of peak height by peak width at one-half peak height. In this manner, the areas of the peaks corresponding to **8a**, **8b**, **8c**, and 1-phenylhexane were determined and tabulated. The ratios of the isomers were calculated and compared for each of the carbene precursors studied. Subsequent TLC analysis employing an eluent system of benzene–carbon tetrachloride (4:1) revealed that no isomerism of the oxirane substrate **10b** or carbonates **1b** and **1c** occurs under the reaction conditions. Furthermore, there was no evidence of the related *cis*- or *trans*-oxiranes (**10a** or **10b**, respectively) in either of the carbonate photolysis mixtures.

**Preparation of *meso*-α,α′-Dimethylhydrobenzoin (16).** The procedure reported by Stocker and co-workers involving the addition of 2 mol of methyllithium to benzil was utilized for the preparation of this diol.[49] Two recrystallizations of the crude product from benzene–heptane provided *meso*-$\alpha,\alpha'$-dimethylhydrobenzoin (**16**), mp 120–121° (lit.[49] mp 120–121°).

**Preparation of *meso*-$\alpha,\alpha'$-Dimethylhydrobenzoin Carbonate (1d).** A solution of 500 mg (1.90 mmol) of *meso*-$\alpha,\alpha'$-dimethylhydrobenzoin (**16**) was heated under reflux with 10 mg (0.10 mmol) of sodium methoxide and 250 mg (2.10 mmol) of diethyl carbonate in 30 ml of anhydrous toluene for 2 hr following the method outlined by Sarel and co-workers.[15] The ethanol which is formed was distilled and collected. The toluene and excess diethyl carbonate were removed under reduced pressure, and the resulting residue was dissolved in methylene chloride and worked up in the manner previously described for **1b**. A total of 200 mg (99%) of *meso*-$\alpha,\alpha'$-dimethylhydrobenzoin carbonate (**1d**), mp 129–130° (lit.[16] mp 129.5–130°), was obtained.

**Preparation of *dl*-$\alpha,\alpha'$-Dimethylhydrobenzoin (17).** This pinacol was prepared by the addition of freshly distilled biacetyl to phenyllithium as outlined by Stocker and co-workers.[49] Several recrystallizations of the crude product from heptane were required to obtain the diol in the desired state of purity, mp 124–125° (lit.[49] mp 124–125°).

**Preparation of *dl*-$\alpha,\alpha'$-Dimethylhydrobenzoin Carbonate (1e).** The procedure used for the preparation of **1e** is a modification of that described by Ludwig and Piech.[14] A solution containing 1.12 g (4.60 mmol) of *dl*-$\alpha,\alpha'$-dimethylhydrobenzoin (**17**) and 0.90 g (11.6 mmol) of anhydrous pyridine in 30 ml of anhydrous benzene was placed in a three-necked round-bottom flask, and a 5.92-g aliquot of a cold solution of 12.5% phosgene in benzene was added dropwise at a rate sufficient to maintain the reaction temperature below 30°. The resulting mixture was stirred overnight and isolation achieved in the manner described previously for **1c**. A total of 0.41 g (37%) of the desired *dl*-$\alpha,\alpha'$-dimethylhydrobenzoin carbonate (**1e**), mp 119–120° (lit.[16] mp 120.5–121°), was obtained.

**Irradiation of *meso*-$\alpha,\alpha'$-Dimethylhydrobenzoin Carbonate (1d) in Methanol.** A solution of 0.027 mg ($1 \times 10^{-4}$ mol) of *meso*-$\alpha,\alpha'$-dimethylhydrobenzoin carbonate (**1d**) in 10 ml of methanol was degassed by nitrogen sparging and irradiated in a quartz tube (254 nm, Hanovia 250 W) for 2 hr. The reaction mixture was concentrated under reduced pressure and examined by GLC [2% OV-17 on Chromosorb W, ⅛ in. × 6 ft (6 mm × 2 m), 110°C]. Two products were observed and determined to be $\alpha$-phenethyl methyl ether and acetophenone in the ratio of 2:1 The yield of $\alpha$-phenethyl methyl ether was determined to be 20% using phenylcyclohexane as an internal GLC standard.

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**Registry No.**—**1a**, 15855-93-3; **1b**, 19456-17-8; **1c**, 28521-60-0; **5**, 470-35-9; **6b**, 579-43-1; **6b**, 655-48-1; **8a**, 7653-96-5; **8b**, 25181-26-4; **8c**, 7653-95-4; **10b**, 1439-07-2; **14**, 19455-94-8; **15**, 28521-61-1; tetraphenylethylene, 632-51-9; diphenylcarbene, 3129-17-7; *trans*-stilbene, 103-30-0; phenylcarbene, 3101-08-4.

## References and Notes

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(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) *Tetrahedron Lett.*, 663 (1970).

(3) (a) Taken in part from the Dissertation in partial fulfillment for the requirements of a Ph.D. degree of R. L. Smith, University of New Orleans, 1971; (b) National Science Foundation Predoctoral Trainee from Sept 1968 to Sept 1969 (GZ 846); National Science Graduate Fellow from Sept 1969 to Sept 1970 (GZ 1205).

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(9) Properly substituted 1,3-dioxoles also give carbenes upon photolysis through cycloeliminations of the [5 → 4 + 1] rather than [5 → 2 + 2 + 1] type. In this case it is the atom flanked by the oxygen atoms which is extruded in the divalent form. R. M. G. Nair, E. Meyer, and G. W. Griffin, *Angew. Chem.*, **80**, 442 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 462 (1968).

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