

Photolysis of Phenyl diazomethane in Olefinic Matrices. Chemistry of Triplet Phenylcarbene

Robert A. Moss* and Ulf-Helge Dolling

Contribution from the Wright Laboratory, School of Chemistry,
Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903.
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Abstract: Photolysis of phenyl diazomethane in *cis*- (or *trans*) butene leads to nearly stereospecific (>97%) cyclopropanation, accompanied by *ca.* 7%, maximum, of such olefins as 3-benzylbutene-1 and *cis*- and *trans*-5-phenylpentene-2. Dilutions of the butene substrate with either octafluorocyclobutane or 1,3-dienes have little effect on the reaction. Photolyses in frozen *cis*-butene matrices (-160 , -196°) take a dramatically different turn, affording large amounts of olefins (up to 52%) and reduced, less stereospecific, cyclopropanation. Triplet phenylcarbene is suggested to be the key intermediate in the matrix experiments, the olefinic products probably arising *via* abstraction-recombination mechanisms.

Simple carbenes composed only of carbon and hydrogen, *e.g.*, methylene, alkylcarbenes, and arylcarbenes, appear to have triplet ground states, although, as generated by photolysis or thermolysis of diazo compounds, their chemistry appears to be that of singlet excited states.¹ In some cases, singlet-triplet separations small enough to allow substantial thermally mediated population of both states may complicate matters.^{1a}

Much effort has been devoted to observing the triplet state chemistry of these carbenes; at least two approaches are commonly employed. The triplet carbene may be obtained directly by photosensitized decomposition of a suitable precursor. Alternatively, the carbene may be generated as a singlet, but in a medium largely composed of an inert diluent. The singlet carbene is thus made to suffer many fruitless collisions with diluent and, hopefully, to cross to its triplet ground state before meeting a substrate molecule. Both approaches have been applied successfully on occasion, both in vapor and liquid phases. However, there are cases in which photosensitization is impractical and the dilution technique apparently fails.² Present application of the dilution method to the generation of triplet phenylcarbene was also without marked success (see below).

Phenylcarbene has been subjected to extensive investigation. The ground state has been designated as triplet on the basis of matrix isolation esr studies,^{3a} which have been extended to 4°K.^{3b} These experiments have been shown to be independent of carbene precursor in three systems.⁴ An emission spectrum of phenylcarbene has also been obtained.⁵ Extended

Hückel calculations can also be interpreted as supporting a triplet ground state for phenylcarbene.⁶ The C-H insertion and the C=C addition reactions of phenylcarbene have also been studied.⁷⁻⁹ The chemical behavior of phenylcarbene, as generated by photolysis of various phenyloxiranes,⁹ 1,2,3-triphenylcyclopropane,⁹ or phenyl diazomethane,^{7,8} appears to be substantially independent of precursor, and that of a singlet rather than a triplet. Gutsche reported only about 3% nonstereospecificity in the addition of phenylcarbene (photolysis of phenyl diazomethane, cyclohexane solvent) to *trans*-butene and about 2.5% nonstereospecificity in its addition to *cis*-butene.⁷ Closs reported corresponding values of 0.5-1 and 3-5% for experiments in the pure olefins.⁸ The high stereospecificity can be taken as support for a singlet state of the reactive intermediate.^{7,8,10} The results could be consistent with triplet phenylcarbene addition if there was "a very fast ring closure allowing only incomplete rotamer equilibration in the intermediate trimethylene diradical."¹¹ Another important observation was that little (2-5%)⁸ product was derived from insertion of phenylcarbene into the butene C-H bonds.^{7,8} Recently, Scheiner has photolyzed 5-phenyltetrazolidine anion in the 2-butenes and observed cyclopropane formation with enhanced nonstereospecificity (6-10% from *cis*-butene) which he attributed to intervention of triplet phenylcarbene,¹² formed *via* photosensitized decomposition of intermediate phenyl diazomethane by 5-tetrazolidine anion triplet.¹³

We have subjected the phenylcarbene-2-butene reactions to intensive reexamination. Most importantly, by carrying out these reactions in solid olefinic matrices, triplet phenylcarbene chemistry can be observed. Not

(1) Several recent reviews include: (a) G. L. Closs, *Top. Stereochem.*, **3**, 193 (1968); (b) A. M. Trozzolo, *Accounts Chem. Res.*, **1**, 329 (1968); (c) R. A. Moss, *Chem. Eng. News*, **47**, 60 (June 16, 1969); 50 (June 30, 1969).

(2) The dilution technique does not, for example, give access to triplet cyclopentadienylidene: R. A. Moss and J. R. Przybyla, *J. Org. Chem.*, **33**, 3816 (1968).

(3) (a) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *J. Amer. Chem. Soc.*, **84**, 4991 (1962); E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, *J. Chem. Phys.*, **40**, 2408 (1964); (b) private communication from Professor E. Wasserman.

(4) L. Barash, E. Wasserman, and W. A. Yager, *J. Amer. Chem. Soc.*, **89**, 3931 (1967); R. E. Moser, J. M. Fritsch, and C. N. Matthews, *Chem. Commun.*, 770 (1967).

(5) 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). The spectrum

was presumably that of the triplet and was measured in a matrix at -196° .

(6) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *ibid.*, **90**, 1485 (1968).

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

(8) G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, **86**, 4042 (1964).

(9) H. Dietrich, G. W. Griffin, and R. C. Petterson, *Tetrahedron Lett.*, 153 (1968), and references therein.

(10) P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, **78**, 4496 (1956).

(11) Reference 1a, p 222.

(12) P. Scheiner, *J. Org. Chem.*, **34**, 199 (1969).

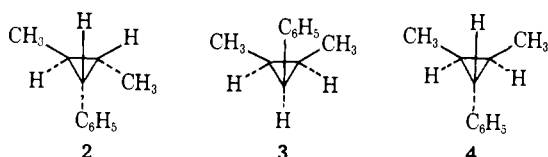
(13) P. Scheiner, *Tetrahedron Lett.*, 4863 (1969).

only is this a result of considerable interest, but the method might have wider application.¹⁴

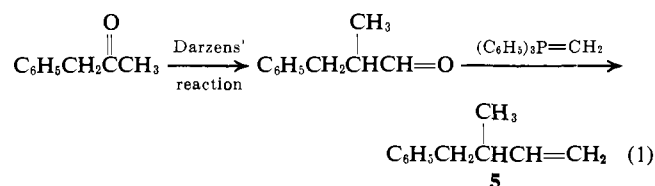
Results

Syntheses. Phenyl diazomethane (**1**) was prepared either by the oxidation of benzaldehyde hydrazone with yellow mercuric oxide,¹⁷ or by the action of sodium methoxide on benzaldehyde tosylhydrazone.⁸ The latter method afforded **1** free of benzaldehyde (ir spectrum). **1** showed no benzaldehyde after 5 months storage over Dry Ice.

Authentic cyclopropanes **2**, **3**, and **4** were prepared from benzal bromide, methyl lithium, and either *trans*- or *cis*-butene, as required.⁸

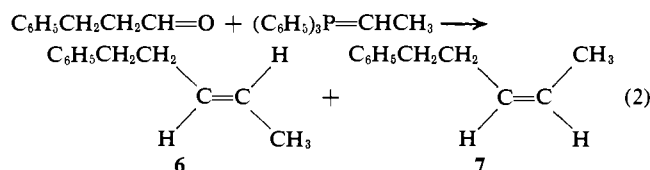


3-Benzylbutene-1 (**5**) was prepared as outlined in eq 1.



The identity of the purified [gas chromatography (gc)] product was established by ir and nmr spectroscopy as well as by elemental and mass spectroscopic analyses.¹⁸

trans-**6** and *cis*-5-phenylpentene-2 (**7**) were obtained from hydrocinnamaldehyde by a Wittig reaction, eq 2.



The product isomer mixture could be laboriously fractionated by iterative gc on a 5% Carbowax 20M column. Purified **6** showed a strong ir absorption at 965 cm⁻¹, characteristic of *trans* 1,2 disubstituted alkenes.¹⁹ *cis*-Olefin (**7**) lacked this band. The ratio, **6**:**7**, was 31:69 as determined by gc on a 100-ft Carbowax K-1540 Golay column. The overall structures of **6** and **7** were determined by ir, nmr, elemental, and mass spectroscopic analyses.¹⁸

Photolyses of 1 in Liquid Olefins. Five studies were elaborated: (1) photolysis of **1** at 0° in pure *cis*-butene; (2) photolysis of **1** at 0° in pure *trans*-butene; (3) photolysis of **1** in *cis*-butene at -100 and -130°; (4) photolysis of **1** at 0° in *cis*-butene diluted with octafluorocyclobutane (C₄F₈); and (5) photolysis of **1** at 0° in *cis*-butene diluted with 1,3-dienes. All irradiations were carried out in Pyrex vessels, under nitrogen or argon, using a 275-W, G. E. sunlamp and a Corning,

(14) Trozzolo has reported carbene chemistry in matrices for H abstraction reactions of diphenylcarbene and benzoylphenylcarbene.^{15,16}

(15) Reference 1b, pp 334-335.

(16) W. A. Gibbons and A. M. Trozzolo, *J. Amer. Chem. Soc.*, **88**, 172 (1965).

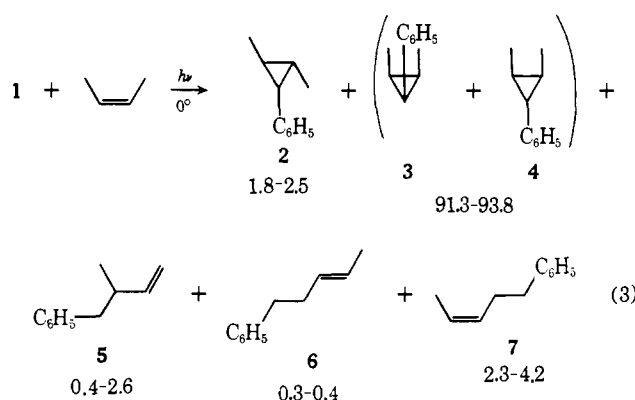
(17) A. Staudinger and A. Gaule, *Chem. Ber.*, **49**, 1897 (1916).

(18) See Experimental Section for details.

(19) R. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Wiley, New York, N. Y., 1958.

C. S. 3-94 uranium glass filter (opaque below 330 mμ). Samples were degassed at 0.01 mm by three freeze (-196°) thaw cycles, with intermediate flushing with argon or purified nitrogen. Typically 0.4-2 mmol of **1** was irradiated in 0.3-0.7 mol of olefin or olefin + diluent. Photolyses were generally not completed, and excess **1** was removed using literature procedures.⁸

Case 1. Six independent photolyses of benzaldehyde-free **1** in *cis*-butene (*trans*-butene <0.1% by capillary gc, column C,²⁰ -50°) were performed at 0°. Irradiation times averaged 3 hr. Recovered *cis*-butene showed no *trans*-butene. Products were identified by gc retention times and augmentation experiments on three different 100-ft Golay columns (A, B, and C²⁰). Product distributions for the C₁₁H₁₄ isomers were obtained by cut-and-weigh integration of gc traces (column A, standardized flame ionization detector). The ranges of product distributions (per cent of C₁₁H₁₄ isomers) over the six experiments are given in eq 3.²¹ As expected, the products of stereospecific addition, *syn*- and *anti*-1-phenyl-*cis*-2,3-di-



methylcyclopropanes (**3** and **4**), are dominant. The *syn*-*anti* ratio (column C) was 1.1-1.2 (lit.⁸ 1.1). The extent of "insertion" or olefin formation was small, in agreement with previous work.^{7,8} Nonstereospecificity, defined as 2/(2 + 3 + 4) × 100, ranged from 1.9 to 2.7%,²² again in accord with literature values.^{7,8} Benzaldehyde was observed (gc, mass spectrum) and was 8-15% of total product (gc peak area) in nondegassed runs. After degassing, benzaldehyde was reduced to 1.3%.

Control experiments demonstrated the stability of the cyclopropanes to reaction conditions. Photolysis of **1** in cyclohexene containing **2**, **3**, and **4** [2/(3 + 4) = 5 × 10⁻³] gave, after normal work-up, a product mixture with an unchanged distribution of **2-4**. No olefins, **5-7**, were detected.

Case 2. Photolysis of **1** in *trans*-butene at 0° gave the following product distribution (cf. formulas in eq 3): **2**, 94.1; (**3** + **4**), 0.5; **5**, 1.7; **6**, 3.7%. Olefin **7** was not seen. Benzaldehyde was 1-2% in this (degassed) run. The *trans*-butene used contained 0.5% *cis*-butene and, therefore, **3** and **4** probably do not

(20) A complete glc column code appears in the Experimental Section.

(21) Details for each run together with standard deviations for each gc analysis will appear in the Ph.D. Thesis of U-H. Dolling.

(22) Phenylcarbene reacts at comparable rates with *cis*- and *trans*-butene.⁹ Since *trans*-butene was less than 0.1% of the *cis*-butene, before and after photolysis, and controls demonstrated product stability, the observed **2** must come from nonstereospecific addition.

Table I. Product Distributions. Photolysis of **1** in *cis*-Butene as a Function of Temperature^a

Temp, °C	2	3	4	5	6	7	$\left(\frac{2 \times 100}{2+3+4}\right)$	$\left(\frac{2+3+4}{5+6+7}\right)$
0	2.1	<i>b</i>	92.7	1.4	0.4	3.5	2.02	17.9
-100°	0.9	51.6	42.2	3.9		1.1	1.0	18.9
-130°	0.5	50.9	43.2	4.7	0.2	1.3	0.6	15.8

^a Data are per cent of products 2-7. Averaged distributions are not renormalized to 100%. ^b Sum of 3 + 4 indicated. ^c Analyses on column A. Benzaldehyde yield was *ca.* 5% in these runs.

reflect nonstereospecific addition. Starting olefin did not isomerize during the photolysis.

Case 3. Photolyses of **1** in *cis*-butene were also conducted at -100 and -130° using a pentane-liquid nitrogen coolant. Table I gives the average product distributions (two runs at each temperature).²¹ For convenience, the *average* distributions for the six 0° experiments (case 1) are also included. There are small changes which appear to exceed the analytical tolerances and reproducibility (*ca.* ±0.5%); however, no large variations are seen as a function of temperature. This is highlighted on comparison of these experiments with those conducted on frozen samples (see below).

Case 4. Photolyses of **1** in *cis*-butene, diluted with C₄F₈, were done at 0° and the stereospecificity data appear in Table II. Mole fractions of **1** ranged from

Table II. Stereospecificity of Addition of Phenylcarbene to *cis*-Butene in the Presence of C₄F₈, 0°^a

Run	X _{C₄F₈}	$\left(\frac{2 \times 100}{2+3+4}\right)$
1	0.911	2.6
2	0.970	3.2
3	0.972	2.7
4	0.992	4.7
5	0.994	2.6
6	0.996	4.7
7 ^b	0.000	2.0

^a Analyses on columns A or C or both [with good (±0.2) agreement]. ^b No diluent, *cf.* Table I.

0.9 to 9×10^{-3} without noticeable effect on the reaction stereospecificity. In run 5, a complete product distribution was obtained. The values were within the ranges observed in the undiluted *cis*-butene experiments, eq 3.

At high dilution there appears to be little or no increase in nonstereospecificity of the phenylcarbene-*cis*-butene reaction. Attempts to study the reaction at X_{C₄F₈} = 0.998 were unsuccessful because insufficient product was obtained. Benzaldehyde was a major product in these experiments. However, a run (X_{C₄F₈} = 0.994) carried out after rigorous degassing (*ca.* 10⁻⁴ mm) reduced benzaldehyde to 5.5% with no significant change in product distribution or nonstereospecificity.

Case 5. Photolyses of **1** in *cis*-butene, diluted with 1,3-butadiene or 2,5-dimethylhexadiene-2,4, were also done at 0°. Use of the purified hexadiene (mole fraction, 0.6) as diluent gave *no* decrease in nonstereospecificity. Thus, photolysis of 80 mg of **1** in the degassed olefin-diene mixture led to $(2 \times 100)/(2+3+4) = 2.7$ (column C). This is to be compared with 2.02 (Table I), the average value for the pure *cis*-butene runs. A control experiment showed that the

2-4 distribution was not changed during removal of the diene after photolysis (distillation at 41° (16-17 mm)).

A similar experiment was carried out using a mixture of 1,3-butadiene and *cis*-butene (mole fractions, 0.549 and 0.449, respectively; the remainder was **1**). Photolysis for 2.5 hr, followed by work-up and analysis on column B, gave the nonstereospecificity ratio as 2.7. Again, no decrease of this ratio was observed. The distribution of 2-7 was also unchanged. In the 1,3-butadiene experiments, a major portion (*ca.* 70%) of product was apparently derived from reaction of phenylcarbene with the diene.

Photolyses of 1 in Solid Butene Olefins. **1** was photolyzed in crystalline matrices of *cis*-butene²³ at temperatures of -160 and -196°. Coolants were isopentane-liquid nitrogen and liquid nitrogen, respectively. Experiments were carried out in Pyrex tubes, fitted with Teflon vacuum stopcocks, after degassing, and under an inert atmosphere. The tubes were suspended in a transparent Dewar flask and were rotated. Photolyses with the G.E. sunlamp and uranium glass filter were carried out in cycles of 30-min irradiation, followed by thawing and homogenizing in the dark at -78°, followed by refreezing. Reactions were extended for total irradiation times of 2-30 hr. Product distributions appear in Table III.

A control experiment, in which **1**, **2**, **3**, and **4** were photolyzed in cyclohexene at -196°, demonstrated that these products were not altered by reaction and work-up conditions. Similar controls showed that *cis*-olefin (**7**) did not isomerize to its *trans* isomer, **6**, or to **5**. *trans*-Butene was not detected (<0.1%) in the *cis*-butene substrate either before or after photolysis.

Product identities were established in several ways. Addition of a -196° product mixture to 5 ml of methanol at -78° followed by dropwise addition of a solution of ozone in methanol (-78°) to a KI-starch end point revealed, after work-up and analysis on column A, only traces of olefins 5-7. Cyclopropanes 2-4 survived.

"Preparative" photolysis of **1** in *cis*-butene at -196° for 30 hr gave **2**, **3**, **5**, and a fraction containing (**4** + **6** + **7**), after gc on column F at 95°. Pure **7** was obtained on column G at 100° and was identical in mass spectral cracking pattern with authentic **7**. Mass spectra-gc experiments on the other fractions (columns G and B) gave proper parent ions and base ions (*m/e* 146 and 91) for 2-6. Satisfactory gc augmentation experiments, using authentic compounds, were carried out for products 2-7 on Golay columns A, B, and C. Benzaldehyde was identified by gc-mass spectrum and gc augmentation.

(23) The melting point of pure *cis*-butene is -138.9°: "Handbook of Chemistry and Physics," R. C. Weast, Ed., 45th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, p C-231.

Table III. Product Distributions. Photolysis of **1** in Solid *cis*-Butene^a

Run	Temp, °C	2	(3 + 4)	5	6	7	$\left(\frac{2 \times 100}{2 + 3 + 4}\right)$	$\left(\frac{2 + 3 + 4}{5 + 6 + 7}\right)$	C ₆ H ₅ CHO
1	-160	1.7	65.7	26.5		6.1	2.6	2.1	<i>b</i>
2	-160	1.9	58.2	26.0	3.2	10.7	3.2	1.5	26.9 ^c
3	-160	2.0	62.2	25.3	2.2	8.2	3.1	1.8	21.7
4	-196	4.4	45.0 ^d	13.7	6.7	30.2	9.0	0.98	<i>b</i>
5	-196	4.3	40.0	17.6	6.0	32.1	9.7	0.80	20.9
6	-196	2.0	46.4	19.7	3.3	28.4	4.1	0.94	12.8
7	-196	3.0	41.7	20.7	4.9	29.7	6.8	0.81	13.0
8	-196	2.3	47.6	20.8	3.4	24.8	4.5	1.0	22.9
8 ^e	-196	2.0	46.0	22.4	3.8	25.8 ^f	4.1	0.92	<i>b</i>

^a Mole fraction of **1** varied from 0.9×10^{-2} to 8×10^{-2} with no significant change in distributions. Data for 2-7 are per cent based on the sum 2-7 as 100%. Each experiment was analyzed on column A from 2 to 7 times. Average standard deviations²¹ for the analyses were: 0.7, 1.6, 1.6, 0.8, and 1.9 for the 2-7 data, as entered. ^b Not analyzed. ^c Peak weight of benzaldehyde to total of 2-7 + benzaldehyde, as per cent. ^d Syn-anti ratio (3/4) was 1.1 in this run. ^e Analysis on column B. ^f Small amounts (to 2% at -160°) of two unknown components, retention times slightly shorter than 6 on column B, were observed. At -196° one of these amounted to 10% of 2-7.

Table IV. Product Distributions. Photolysis of **1** in *cis*-Butene and C₄F₈ at Various Temperatures^a

Temp, °C	X _{C₄F₈}	2	(3 + 4)	5	6	7	$\left(\frac{2 \times 100}{2 + 3 + 4}\right)$	$\left(\frac{2 + 3 + 4}{5 + 6 + 7}\right)$
0	0.994	2.5	94.4	0.7	0.3	2.2	2.6	30.3
-70	0.987	0.3	96.9	0.3		2.5	0.3	34.7
-130	0.985	1.2	85.4	4.6		9.2	1.4	6.1
-160	0.988	0.9	64.0	8.8		26.4	1.4	1.8
-196	0.989	0.3	38.1	9.8	1.5	50.3	0.8	0.6

^a Data are per cent of total products, 2-7. Each run was normalized to 100%, but averages of runs are not renormalized.

Comparison of the 0 to -130° results (Table I) with those at -160 and -196° (Table III) reveals dramatic and significant alterations in product distribution which appear when the reaction phase is changed from liquid to solid. Cyclopropanes **2-4** decrease, while olefins **5-7** become important products. Quantitatively, total cyclopropanes-total olefins changes from (16-19):1 in the liquid runs to (1.5-2):1 in the -160° solid runs and decreases further to about (0.8-1):1 in the -196° solid runs. Also striking is the increase in benzaldehyde yield. Liquid runs yield little of the aldehyde (1-2%); however, the solid runs afford 12-27% of this product, even after degassing (Table III). This does not represent a gradual buildup of the aldehyde during the course of the matrix photolyses, as product distribution was shown to be essentially independent of photolysis time over 1.5 to 30 hr.

Comparison of the -160 and -196° matrix studies reveals further trends. The nonstereospecificity undergoes a small but significant increase (maximum, *ca.* 9-10%). A further decrease in the cyclopropanes-olefins ratio is observed, olefins now being dominant products. Most strikingly, the distribution between olefins **5** and the isomer pair **6** and **7** has reversed, **7** strongly dominating at -196°.

Photolysis of **1** in *trans*-butene at -196° afforded the distribution: **2**, 69.5; **3**, 1.7; **4**, 2.2; **5**, 16.1; **6**, 4.2; and **7**, 6.6%, as analyzed on column B. Comparison with the 0° *trans*-butene experiment (see above) reveals a decrease in cyclopropane **2**, a small but significant advent of nonstereospecific addition products **3** and **4**, and important increases in olefins **5-7**. Benzaldehyde formed in 38% yield, as opposed to the 0° *trans*-butene experiment where it was only 1-2%.

The -196° *cis*-butene product mixtures were inspected (gc) for other components. Toluene (double abstraction product of triplet phenylcarbene) was

absent both in 0 and -196° photolyses. Bibenzyl was present in about 1% yield in the 0° products, but absent from the -196° matrix products. *trans*-Stilbene was formed under both conditions, but seemed more important in the -196° products. Other long retention time products not investigated may have included *cis*-stilbene and the azine derived from **1**.⁸

Low-temperature photolyses of **1** were also done in mixed matrices composed of *cis*-butene and C₄F₈. Results are given in Table IV. They represent single runs at 0 and -130°, the average values of duplicate runs at -70 and -160°, and of three runs at -196°. (Standard deviations were similar to those given in footnote *a* of Table III.) Although these reaction mixtures appear solid at -130 and -70°, both temperatures are above the melting point of *cis*-butene²³ and the exact state of the olefin in these matrices is unknown. Nevertheless, note the apparent increase in stereospecificity as temperature is lowered to -196°. This contrasts with results for undiluted *cis*-butene matrices (Table III). Most striking in Table IV is the extreme dominance of olefin **7** at -196°. Moreover, **7** exceeds **5** under all conditions in these experiments, whereas in pure *cis*-butene matrices, **5** exceeds **7** at -160°. Note also the absence of *trans*-olefin **6** (compare, Table III). Benzaldehyde was the major product at -196°, exceeding the total of 2-7 in one run. Some of these effects may reflect the comparative hardness of *cis*-butene and C₄F₈-*cis*-butene matrices, and the attendant relative ease of rotations around single bonds in allylic and 1,3-diradicals, as well as the freedom for relative motion of members of radical pairs within the matrices.

Discussion

Attempts to capture triplet phenylcarbene in liquid-phase dilution experiments gave little or no increase in

nonstereospecificity and no significant increases in olefin yield at high dilution with C_4F_8 . These results parallel earlier failures in studies of cyclopentadienylidene^{2,24} and the related 4,4-dimethylcyclohexadienylidene.^{25,26} A tentative conclusion is that photolysis of **1** gives singlet phenylcarbene, the reactivity of which is too great to permit observation of triplet phenylcarbene chemistry within the present practical range of dilution experiments.²⁷

The *cis*-butene + **1** photolysis is altered dramatically when the reaction is carried out in the solid state. Table V lists the averaged product distributions of the

Table V. Average Product Distributions. Photolysis of **1** in *cis*-Butene at 0, -160, and -196°^a

Temp, °C	2	(3 + 4)	5	6	7	$\left(\frac{2 \times 100}{2+3+4}\right)$	$\left(\frac{2+3+4}{5+6+7}\right)$
0 ^b	2.1	92.7	1.4	0.4	3.5	2.02	17.9
-160 ^c	1.9	62.0	25.9	2.7	8.3	3.0	1.7
-196 ^d	3.2	43.9	18.5	4.9	29.0	6.8	0.9

^a Data are per cent of total 2-7 normalized to 100% in each run; these averaged distributions are not renormalized. ^b Liquid phase. Standard deviations are: 0.3, 1.1, 1.0, 0.1, and 0.6. ^c Solid phase. Standard deviations are: 0.2, 3.8, 0.6, 0.5, 2.3, and 0.3. ^d Solid phase. Standard deviations are: 1.1, 3.2, 3.0, 1.5, 2.7, and 2.5.

six 0° liquid-phase photolyses, and of the three -160° and five -196° solid-phase photolyses (detailed in Table III).

The results of Table V pose three questions. (1) Does the emerging dominance of olefins 5-7 in the solid-phase experiments signal dominant triplet phenylcarbene chemistry? (2) How are 5-7 formed? (3) If the answer to **1** is affirmative, how does the matrix effect operate to select for triplet chemistry?

(1) The first question may be answered affirmatively, based on analogy of product type to many other systems in which triplet carbene chemistry seems to have been observed. We will note especially examples of H atom abstraction attributed to triplet carbenes, since we believe (see below) that such reactions are involved in the formation of 5-7.

Products analogous to **5** and **6** have long been associated with triplet CH_2 chemistry in both gas and liquid phases.²⁹ Not only does triplet CH_2 abstract hydrogen atoms³⁰ but also, apparently, methyl radicals.³¹ Other carbenes which abstract H atoms include triplet dicyanocarbene³² and triplet biscarbome-

(24) A brief review of the generation of triplet carbenes in the liquid phase is given in ref 2.

(25) M. Jones, Jr., A. M. Harrison, and K. R. Rettig, *J. Amer. Chem. Soc.*, **91**, 7462 (1969).

(26) Dilution experiments succeed when the gem dimethyl group is replaced with a carbonyl group (in 3,5-di-*tert*-butyl-4-ketocyclohexadienylidene): W. H. Pirkle and G. F. Koser, *Tetrahedron Lett.*, 3959 (1969).

(27) Analogous behavior is expected of methylene. However, photolysis of CH_2N_2 in *cis*-butene, diluted with a 200-fold excess of C_3F_8 , is reported to give triplet methylene chemistry, increased nonstereospecific addition and *trans*-2-pentene being detected.²⁸

(28) D. F. Ring and B. S. Rabinovitch, *J. Phys. Chem.*, **72**, 191 (1968); *Int. J. Chem. Kinet.*, **1**, 11 (1969).

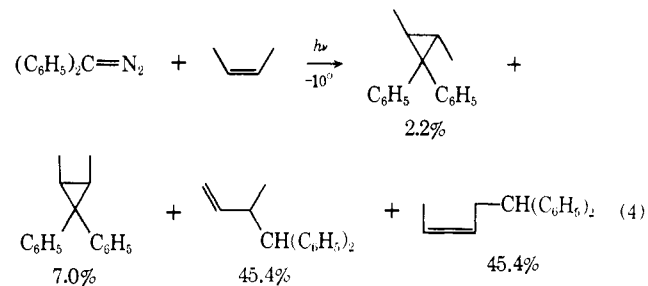
(29) For a review, see ref 1a, pp 210-219. A more recent representative contribution is: T. W. Eder and R. W. Carr, Jr., *J. Phys. Chem.*, **73**, 2074 (1969).

(30) For example, D. F. Ring and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, **88**, 4285 (1966).

(31) H. M. Frey and R. Walsh, *Chem. Commun.*, 158, 159 (1969).

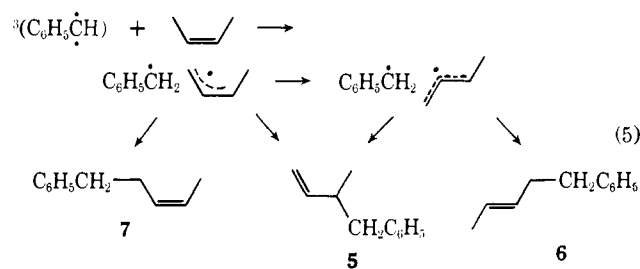
(32) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 1979 (1966).

thoxycarbene,³³ though these reactions are efficient only with alkanes, not with alkenes. Abstraction reactions of triplet dibenzocycloheptylidene and related species have been demonstrated by Moritani's group.³⁴ Other important examples include H atom abstraction by such triplet species as phenylketocarbene,³⁵ phenylferrocenylcarbene,³⁶ and carbenes derived from diazoanthraquinone^{37,38} and related species.³⁸ A final and striking analogy to our matrix photolysis product distributions comes from studies of triplet diphenylcarbene-*cis*-butene reactions. That H abstraction is common in diphenylcarbene reactions has long been known,^{1a,39-41} but the detailed distribution summarized in eq 4² is particularly noteworthy. The olefinic products are attributed to abstraction-re-



combination reactions^{1a,13} of triplet diphenylcarbene. Analogy to our matrix experiments (Table V) is clear, though olefins dominate more markedly, and nonstereospecificity is somewhat greater, in the diphenylcarbene work. Also, no *trans* olefin, analogous to **6**, is reported.

(2) We suggest the mechanism of eq 5 to rationalize formation of 5-7 in the matrix experiments. In the



matrix environment, the radical pairs should collapse with high efficiency. No trace of products derived from free benzyl radicals, such as bibenzyl or toluene,

(33) M. Jones, Jr., W. Ando, and A. Kulczycki, Jr., *Tetrahedron Lett.*, 1391 (1967).

(34) I. Moritani, S-I. Murahashi, H. Ashitaka, K. Kimura, and H. Tsubomura, *J. Amer. Chem. Soc.*, **90**, 5918 (1968), and references therein.

(35) D. O. Cowan, M. C. Couch, K. R. Kopecky, and G. S. Hammond, *J. Org. Chem.*, **29**, 1922 (1964); A. Padwa and R. Layton, *Tetrahedron Lett.*, 2167 (1965); B. M. Trost, *J. Amer. Chem. Soc.*, **88**, 1587 (1966).

(36) A. Sonoda, I. Moritani, T. Saraie, and T. Wada, *Tetrahedron Lett.*, 2943 (1969).

(37) G. Cauquis and G. Reverdy, *ibid.*, 1085 (1968); 1493 (1967).

(38) J. C. Fleming and H. Schechter, *J. Org. Chem.*, **34**, 3962 (1969).

(39) W. Kirmse, L. Horner, and H. Hoffmann, *Ann.*, **614**, 19 (1958).

(40) G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962).

(41) D. R. Dalton and S. A. Liebman, *Tetrahedron*, **25**, 3321 (1969).

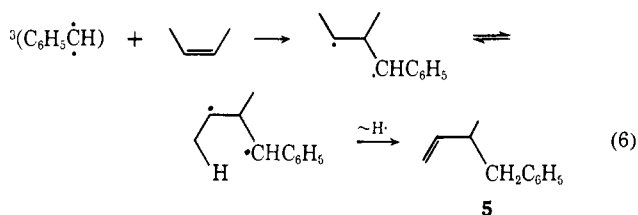
(42) G. L. Closs and L. E. Closs, unpublished work; private communication from Professor G. L. Closs.

(43) Physical evidence for such reactions follows from CIDNP experiments: G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **91**, 4549 (1969). CIDNP experiments also indicate that triplet phenylcarbene reacts with diphenylmethane affording 1,1,2-triphenylethane by abstraction-recombination; private communication from Professor G. L. Closs.

was detected. This contrasts to liquid-phase experiments with triplet diphenylcarbene³⁹⁻⁴² and biscarbomethoxycarbene,³³ where products analogous to bibenzyl are prominent. Note, also, that in the colder and presumably harder -196° matrix, **7** increases at least partly at the expense of **5**. Whereas **7** can form *via* abstraction-recombination with a minimum of intraradical pair motion, **5** requires such motion and should be disfavored.

The presence of triplet phenylcarbene also accounts for the somewhat greater nonstereospecificity observed in cyclopropane formation at -160 and -196° ,⁴⁴ and for the marked formation of benzaldehyde from traces of oxygen still present in the degassed systems.

It is possible that some **5** arises *via* eq 6, a mechanism suggested for olefin formation with triplet methylene and *cis*-butene.^{1a} This mechanism could not here



account for **6** or **7**.⁴⁵ Finally, in Scheiner's suspected generation of triplet phenylcarbene in *cis*-butene solution, products such as **5-7** may also have formed.⁴⁶

(3) The mechanism by which the matrix induces triplet phenylcarbene chemistry is uncertain. An obvious possibility is that the singlet carbene is formed initially but, restricted in the matrix, decays to the triplet at least as fast as it reacts with the matrix.⁴⁷ The details of such a process are not well defined.

There is a clear possibility, however, that a rapid, thermally driven, singlet-triplet equilibrium is involved in phenylcarbene reactions, as it apparently is in diphenylcarbene reactions.^{1a} This may seem unlikely, since the comparative chemistry of phenyl- and diphenylcarbenes appears to differ so markedly in solution. However it cannot be excluded, particularly because some of the effects of temperature on the stereospecificity of diphenylcarbene addition reactions^{1a,42} seem to parallel our observations for phenylcarbene at -100 and -130° (see above, Table I). If triplet and singlet phenylcarbene turn out to be nearly isoenergetic, then the matrix effect would have to be understood in terms of its effects on the kinetics of the competitive singlet and triplet carbene processes occurring within it.

The concept of a rapid singlet-triplet equilibrium would also have the advantage of explaining the small degree of nonstereospecificity at 0° (singlet addition >

(44) The exact temperature at which our reactions occur is not known precisely. They could be complete at the temperature of the photolyses, -160 or -196° , or they could lead to radical pairs which do not complete reaction until the thawing periods, -196 to -70° . The significant differences between our -160 and -196° matrix results suggest, however, that much of the product formation occurs in the matrices and near the photolyses temperatures.

(45) Other rearrangement products could form from the putative trimethylene diradical of eq 6, such as $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_5$ and $\text{CH}_3\text{CH}=\text{CH}-\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$. These may have been formed to a small extent (see Table III, footnote *f*), but definite evidence is lacking.

(46) References 12 and 13 and private communication from Professor Scheiner.

(47) Some of the **3**, **4**, and **7** observed at -160 and -196° can come from the singlet carbene.

triplet addition). It would explain the failure of C_4F_8 and 1,3-diene additives to affect this nonstereospecificity (assuming that these additives do not greatly perturb the equilibrium).^{48a}

In conclusion, we believe that photolysis of **1** in frozen 2-butenes leads to triplet phenylcarbene, which reacts by abstraction-recombination and $\text{C}=\text{C}$ addition pathways.^{48b} The technique is the first well-characterized method for detecting such chemistry and could be applicable to other carbenes as well.

Experimental Section

Instruments. Ir spectra were recorded on a Perkin-Elmer Model 137 spectrometer. Nmr spectra were recorded on a Varian A-60 spectrometer as CCl_4 solutions with an internal $(\text{CH}_3)_4\text{Si}$ standard. A Hitachi Perkin-Elmer RMU-7 mass spectrometer (in conjunction with a Perkin-Elmer Model 881 gas chromatograph, where required) was used. Product distributions were generally determined on a Barber-Colman Series 5000 gas chromatograph, which was equipped with a flame ionization detector. Preparative gc made use of a Varian-Aerograph A90-P3 instrument. The following code applies to gc columns: column A, 100 ft \times 0.01 in., wall coated, purified Apeizon-L, open tubular column; column B, 100 ft \times 0.01 in., wall coated, Carbowax K-1540, open tubular column; column C, 100 ft \times 0.01 in., wall coated, SF-96, open tubular column; column D, 12 ft \times 0.25 in., 15% SF-96 on 45-60 Gas-Chrom R; column E, 12 ft \times 0.25 in., 5% Carbowax 20M on 90-100 Anakrom ABS; column F, 10 ft \times 0.25 in., 10% SE-30 on 45-60 Gas-Chrom R; column G, 20 ft \times 0.125 in., 4.5% Apeizon-L on 60-80 Chromosorb G.

Materials. The following reagents were obtained from Matheson Co., and were C.P. grade unless otherwise indicated: *cis*-butene, *trans*-butene, 1,3-butadiene, 2,5-dimethylhexadiene-2,4, octafluorocyclobutane, benzyl methyl ketone, ethyl chloroacetate, sodium ethoxide (practical), triphenylphosphine, and hydrocinnamaldehyde (practical). Olefins were checked for purity by gc and used as received. Phenyllithium, 2.2 M in 30:70 (v/v) ether-benzene, was obtained from Lithium Co. of America. Phenyl diazomethane and cyclopropanes **2-4** were prepared by literature methods (see above). The cyclopropanes were purified on column D (140°); their nmr spectra agreed with reported spectra.⁸

3-Benzylbutene-1 (5). To a solution of 0.3 mol of benzyl methyl ketone and 0.3 mol of ethyl chloroacetate in 60 ml of benzene (dried over sodium), 0.36 mol of practical grade sodium ethoxide powder was added with stirring over a period of 1 hr. The temperature was kept at $15-20^\circ$. After 2 additional hr of stirring at ambient temperature, the mixture was poured over 250 g of crushed ice. The organic layer was separated and the aqueous layer was extracted with 100 ml of benzene. The combined benzene solutions were washed three times with 100-ml portions of water, the last portion containing 4 ml of acetic acid. The solution was dried over MgSO_4 , filtered, and concentrated on a rotary evaporator. The residue was distilled over a Vigreux column and the fraction with bp $148-151^\circ$ (7 mm) (43 g, 65%) was collected: ir (neat) 3.35 m, 5.74 s, 6.7 m, 7.1 m, 7.26 m, 8.35 m, 9.25 m, 9.7 m, 13.4 m, 14.33 m μ .

The ester (0.183 mol) was hydrolyzed with 0.19 mol of sodium ethoxide in a solution of 80 ml of ethanol and 4.5 ml of water. The sodium salt of the glycidic acid separated and was collected by filtration and washed with 15 ml of ethanol followed by 15 ml of ether. The salt was added to 70 ml of 2 M HCl and the mixture was refluxed for 2 hr. The separated oil was extracted with 50 ml of benzene. The extract was washed with 60 ml of water. Distillation of the extract afforded the crude 2-benzylpropanal at $80-85^\circ$ (10 mm). Purification⁴⁹ was effected by washing a benzene solution of the aldehyde with 5% sodium carbonate solution, formation of the sodium bisulfite derivative, and liberation of the aldehyde with refluxing 5% sodium carbonate solution. The aldehyde was washed with *ca.* 10 ml of water and dried over molec-

(48) (a) We thank a referee for emphasizing these points. (b) Reactions of phenylcarbene in an isobutylene matrix apparently take a related course: R. A. Moss and U. H. Dolling, unpublished work.

(49) The overall procedure follows A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1966, p 907. The purification follows Ramart-Lucas and M. L. Labaune, *Justus Liebigs Ann. Chem.*, [10] 16, 276 (1931).

ular sieve. The yield was 4 g (15%), based on glycidic ester. The aldehyde autoxidized upon standing. The semicarbazone had mp 120° (lit.⁵⁰ 123°). Spectroscopic samples were obtained by gc on column F: ir (neat), *inter alia*: 3.58, 3.70 (O=C—H), 5.83 (C=O) μ ; nmr doublet, 9.47, $J = 1.5$ Hz (aldehyde proton); narrow multiplet, 7.07 (phenyl); multiplet, 3.03–2.37 (benzyl and carbonyl); doublet, 0.98, $J = 6.5$ Hz (methyl).⁵¹

To a stirred suspension of 30 mmol of triphenylmethylphosphonium bromide⁵² in 70 ml of dry ether was added 30 mmol of phenyllithium in ether–benzene (30:70, v/v), dropwise, over 15 min. The resulting red solution was stirred for 4 hr at ambient temperature. A solution of 4.45 g of freshly distilled 2-benzylpropanal in 25 ml of dry ether was added dropwise over 15 min. A white solid (triphenylphosphine oxide) precipitated and the solution bleached. The reaction mixture was refluxed for *ca.* 15 hr, cooled, and filtered. The solid was washed with 100 ml of ether, which was then added to the filtrate. The combined solution was washed four times with 100-ml portions of water (until neutral to litmus), dried over CaCl₂, and concentrated on the rotary evaporator. The residue was distilled and 3-benzylbutene-1 was collected at 59–61° (8 mm). The yield was 3.4 g (78%, based on the aldehyde). Spectroscopic and analytical samples were purified by gc on column E at 120°: ir (neat) 3.25, 3.30, 3.36, 3.42 (s, vinyl and aryl), 6.10 s (C=C), 6.22 m, 6.30 w, 6.70 s, 6.89 s, 7.09 m, 7.30 m μ ; other strong broad bands appeared at 10.05, 10.95, 13.50, and 14.35 μ ; nmr⁵¹ "singlet," 7.05 (aryl); multiplet, centered at 5.72 (vinyl); crude quartet, 4.95 (=CH₂); crude triplet, 4.73 (=CH₂); multiplet, centered at *ca.* 2.5 (benzyl + carbonyl); doublet, 0.88, $J = 6.5$ Hz (methyl).

Anal. Calcd for C₁₁H₁₄: C, 90.35; H, 9.65. Found: C, 90.66; H, 9.54.⁵³

5-Phenylpentene-2, *trans*-6, and *cis*-7. Triphenylethylphosphonium iodide was prepared from 0.105 mol of triphenylphosphine and 0.148 mol of ethyl iodide. We obtained 38.8 g (88%) of product, mp 169–170°, lit.⁵⁴ 164–165°.

Hydrocinnamaldehyde was rectified by distillation over an 8-cm Vigreux column and the fraction, bp 89–92° (7 mm), was collected. A Wittig reaction employing this aldehyde and the triphenylethyl-

phosphonium iodide was run using the procedure described above for 3-benzylbutene-1. The following quantities were used: 50 mmol of triphenylethylphosphonium iodide in 100 ml of dry ether, 50 mmol of phenyllithium (22.7 ml of a 2.2 M solution in 30:70 v/v ether–benzene), and 50 mmol of the hydrocinnamaldehyde in 25 ml of dry ether. Crude product was obtained by distillation at 69–72° (7 mm). The yield was 2.7 g (37%) of the isomer mixture 6 and 7 (31:69 by gc on column B at 90°). Repetitive gc on column E at 120° gave separated samples of better than 98% purity (column B): ir, 6 (neat) 3.3 s, 3.42 s, 3.51 s, 5.16 w, 5.38 w, 5.58 w, 5.76 w, 5.98 w, 6.25 m, 6.7 s, 6.9 s, 6.97 m, 7.3 m, 7.45 w, 7.68 w, 9.35 m, 9.72 m, 10.35 s, 13.5 s, 14.4 s (μ); the band at 10.35 μ indicates the *trans* geometry;¹⁹ ir, 7 (neat) 3.25 m, 3.3 s, 3.42 s, 3.5 s, 5.16 w, 5.38 w, 5.58 w, 5.76 w, 6.05 m, 6.25 m, 6.7 s, 6.9 s, 6.97 m, 7.15 m, 7.32 m, 7.55 m, 9.35 m, 9.73 m, 10.1 m, 13.4 s, 14.4 s (μ); nmr (mixture of isomers, purified on column E at 120°)⁵¹ "singlet," 7.06 (aryl); multiplet, centered at 5.35 (vinyl); multiplet, centered at *ca.* 2.50 (benzylic and allylic); crude triplet, 1.56 (methyl).

Anal. Calcd for C₁₁H₁₄: C, 90.35; H, 9.65. Found: C, 90.56; H, 9.34.⁵³

Analytical. The photolysis apparatus, procedure, control experiments, and related details appear above and in Tables I–V. The work-up procedure was similar to the literature method.⁸ Table VI summarizes typical gc retention times of the products

Table VI. Gc Retention Times (Minutes) of Photolysis Products

Column	Retention time of product						C ₆ H ₅ CHO
	2	3	4	5	6	7	
A ^a	13.5	19.8	18.9	11.9	17.1	17.5	8.0
B ^b	16.5	25.9	29.7	14.9	24.6	26.3	31.8
C ^a	7.1	9.0	8.5	6.5	7.7	8.0	5.1

^a Column at 120°, 12 psig N₂ carrier gas. ^b Column at 79°, 12 psig N₂ carrier gas.

under the analytical conditions; refer to the column code above. The Barber–Colman gc was used.

Acknowledgments. We are very grateful to the National Science Foundation (GP-12645), and to the National Institutes of Health (GM-13585), whose financial support made this work possible. We thank Professor S. Toby for help with a degassing experiment.

(50) Reference 49, Ramart-Lucas and Labaune.

(51) Nmr signals are in parts per million downfield from internal (CH₃)₄Si. Integral ratios were approximately correct.

(52) G. Wittig and U. Schöllkopf, *Org. Syn.*, **40**, 66 (1960).

(53) Analyses by Micro-Tech Laboratories, Skokie, Ill.

(54) A. Michaelis and H. v. Soden, *Ann.*, **229**, 295 (1885).