

Addition of Diphenylmethylene to 1,2-Dichloroethylenes. New Chemical Evidence for a Carbene Singlet-Triplet Equilibrium

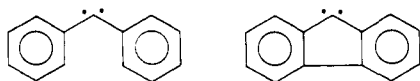
Peter P. Gaspar,*^{1a} Bonnie L. Whitsel,^{1a} Maitland Jones, Jr.,^{1b} and Joseph B. Lambert^{1c}

Contribution from the Department of Chemistry, Washington University, St. Louis, Missouri 63130, the Department of Chemistry, Princeton University, Princeton, New Jersey 08540, and the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received October 19, 1979

Abstract: Addition of diphenylmethylene to *cis*- and *trans*-1,2-dichloroethylene gives the corresponding 1,2-dichloro-3,3-diphenylcyclopropane with greater than 90% stereospecificity. A product of addition with rearrangement, 3,3-dichloro-1,1-diphenyl-1-propene, is also obtained, and this is the major product from *trans* olefin. The cyclopropane product is believed to arise principally from concerted addition by the singlet carbene, while the rearrangement product is assigned to the triplet carbene. This result confirms earlier indications that dihaloethylenes can provide a clear chemical distinction between singlet and triplet carbenes by yielding quite different products from the two spin states. Neither competition from another olefin nor moderation by hexafluorobenzene alters the product ratio from addition of diphenylmethylene to dichloroethylenes, and this is new chemical evidence for the establishment of a singlet-triplet equilibrium for diphenylmethylene under the conditions employed for olefin addition reactions.

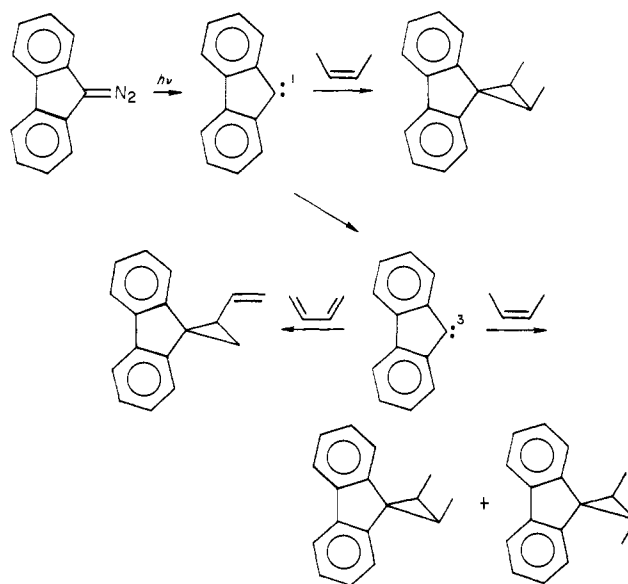
Introduction

The participation of several low-lying electronic states in the chemistry of many carbenes is a factor that has contributed to both the fascination and the complexity of these reaction systems.^{2a,b} Differences in the reactivity of singlet and triplet states of carbenes are well established, and for some carbenes it has been possible to generate them selectively in a particular electronic state.² In general the conversion of one carbene spin state to another, intersystem crossing, is a process that can compete with chemical reactions and makes the assignment of rates and mechanisms to discrete spin states both difficult and controversial. The interconversion of carbene spin states is by no means well understood, and explanations of the apparent differences between such structurally similar molecules as diphenylmethylene and fluorenylidene are only beginning to emerge.³

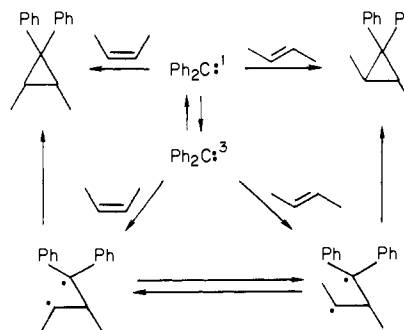


It has been known for some time that photodissociation of diazofluorene produces intermediates that react with olefins largely by addition to form cyclopropanes, a classic carbene reaction.^{4a} The ratio of stereoisomeric cyclopropane products was found to vary with the concentrations of inert diluent and scavengers.^{4b} The decrease in stereospecificity upon dilution is compatible with the formation of a mixture of singlet and triplet fluorenylidene. The singlet is believed to undergo stereospecific *cis* addition to an olefin, but collisions with inert molecules can induce intersystem crossing to the ground-state triplet carbene.⁵ Triplet fluorenylidene can also add to olefins but gives a mixture of cyclopropane stereo-

Scheme I



Scheme II



isomers. The addition of some molecules, including butadiene and oxygen, enhances the stereospecificity of addition. These reagents seem to act as scavengers for triplet fluorenylidene, and thus in their presence a larger fraction of the olefin adduct comes from the singlet carbene. This scavenger effect is in accord with

(1) (a) Washington University; (b) Princeton University; (c) Northwestern University.

(2) (a) P. P. Gaspar and G. S. Hammond in "Carbenes", Vol. II, R. A. Moss and M. Jones, Jr., Eds., Wiley-Interscience, New York, 1975, p 207; (b) H. D. Roth, *Acc. Chem. Res.*, **10**, 85 (1977); (c) W. J. Baron, M. R. DeCamp, M. E. Hendrick, M. Jones, Jr., R. H. Levin, and M. B. Sohn in ref 2a, Vol. I, 1978, p 1.

(3) R. A. Moss and M. A. Joyce, *J. Am. Chem. Soc.*, **100**, 4475 (1978).

(4) (a) A. A. Lamola, B. S. Thesis, Massachusetts Institute of Technology, June 1961; W. v. E. Doering and M. Jones, Jr., *Tetrahedron Lett.* 791 (1963); E. Funakubo, I. Moritani, T. Nagai, S. Nishida, and S.-i. Murahashi, *ibid.*, 1069 (1963); (b) M. Jones, Jr., and K. R. Rettig, *J. Am. Chem. Soc.*, **87**, 4013, 4015 (1965).

(5) A. M. Trozzolo and E. Wasserman in ref 2a, p 185.

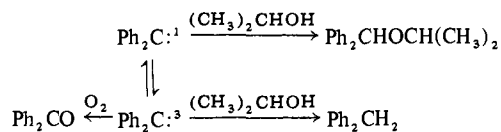
a reaction scheme in which intersystem crossing can compete with reactions of singlet but *not* triplet fluorenylidene^{6,7} (Scheme I).

Diphenylmethylene addition to olefins responds quite differently to the changes in reaction parameters that alter the stereospecificity of fluorenylidene addition.⁸ The stereospecificity of addition of diphenylmethylene to *cis*- and *trans*-2-butene is not affected by dilution or by the presence of oxygen scavenger. These observations have been explained by the suggestion of a singlet-triplet equilibrium for diphenylmethylene.⁹ This reaction scheme incorporates the Skell postulate that singlet carbenes will undergo concerted *cis* addition, while addition of the triplet forms a diradical intermediate whose rapid conformational interconversion leads to a *mixture* of cyclopropane stereoisomers (Scheme II).

If intersystem crossing in both directions is rapid compared to the rate of addition of the carbenes to the olefins and the rate of reaction of carbenes with scavengers, then the stereospecificity of addition should be independent of the concentrations of diluents and scavengers. The ratio of stereoisomers should depend only on the equilibrium constant, on the relative rates of addition of singlet and triplet, and on the partitioning of the biradical intermediate in the addition of the triplet between the isomeric cyclopropanes.

Equilibrium between singlet and triplet diphenylmethylene is also indicated by an elegant kinetic study of its reactions employing flash photolysis and kinetic ultraviolet spectroscopy.¹⁰ The analysis of the rate measurements incorporated a reaction scheme in which rapid singlet-triplet equilibrium was assumed. The kinetic analysis was successful over a wide range of reaction conditions including those under which the carbene disappeared principally by second-order dimerization, by addition to butadiene, and by reaction with methanol. The dimerization and butadiene addition are thought to occur in the triplet state of the carbene, while reaction with methanol is believed to be a singlet-state reaction.

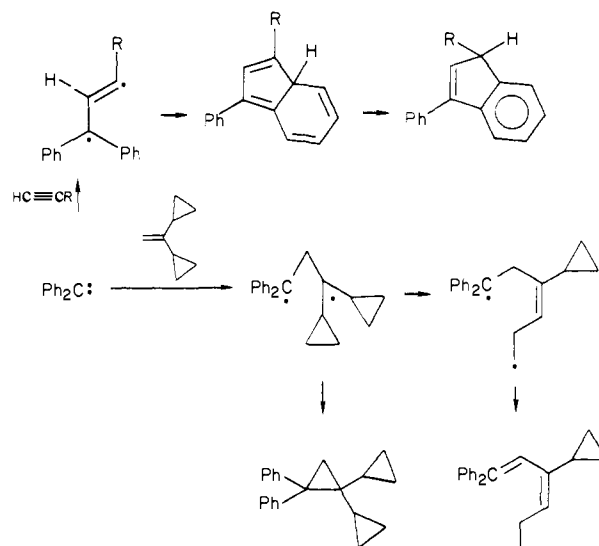
A singlet-triplet equilibrium had been inferred previously by Bethell and co-workers from the observation that the ratio of products attributed to the reactions of singlet and triplet diphenylmethylene, respectively, did not vary with the substrate ratio.¹¹



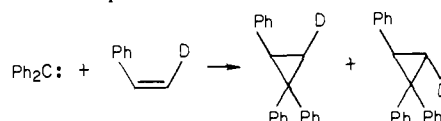
Even earlier Bethell and co-workers had invoked a rapid singlet-triplet equilibrium to explain the competition between a reaction attributed to singlet diphenylmethylene, azine formation, and the hydrogen abstraction believed to involve the triplet carbene.¹² Singlet-triplet equilibria have also been suggested for other carbenes.¹³

While all the experiments on diphenylmethylene cited above have led to observations compatible with a rapid singlet-triplet equilibrium being established under reaction conditions, certain data point in another direction. It has been found that the *cis* to *trans* product ratio from addition of diphenylmethylene to

Scheme III



cis- β -deuteriostyrene decreases from 65:35 in the absence of diluent to ca. 55:45 in the presence of 90 mol % hexafluorobenzene.¹⁴



This corresponds to a change in the ratio of reacting spin states from 30% singlet-70% triplet to 10% singlet-90% triplet.¹⁵ This change suggests that the spin states of the carbene are *not* in equilibrium in the absence of inert moderator, or that there is a solvent effect on the equilibrium constant.

More recently, the isotope effects observed in the reactions of diphenylmethylene with several amines have been interpreted in terms of an *irreversible* conversion of singlet to triplet carbene under the reaction conditions employed.¹⁶

In previous studies of diphenylmethylene it has been difficult to assess the ratio of singlet to triplet carbenes undergoing reaction. The present series of experiments was undertaken in order to employ a new reaction substrate that seemed capable of providing a more direct measure of the ratio of reacting spin states.

Olefins are the only class of substrate for which agreement exists that reaction occurs with *both* singlet and triplet diphenylmethylene. In the past, extreme reliance has been placed on the degree of stereospecificity of carbene addition as the principal criterion for the participation of triplet states in the addition of carbenes to olefins.

Even if one accepts the validity of the Skell postulate that assigns total stereospecificity to cyclopropanation by singlet carbenes and nonstereospecific addition to triplet carbenes, there is a problem in obtaining a quantitative estimate of triplet participation. The degree of nonstereospecificity cannot be converted into a ratio of reacting spin states unless one knows the distribution of stereoisomers from the pure triplet carbene. This is generally not known, and it is interesting that, in the one case that the distribution could be assigned with some confidence,¹⁵ the apparent ratio of diphenylmethylene spin states varied with the reaction conditions. It was therefore considered instructive to examine reactions with a substrate such that triplet diphenylmethylene

(6) Singlet fluorenylidene will of course also undergo addition to butadiene, but the selectivity of the triplet carbene between butadiene and monoolefin is much greater than that of the singlet.

(7) It has recently been found that at very low temperatures triplet fluorenylidene abstracts allylic hydrogen atoms in preference to addition; see ref 3.

(8) The addition of diphenylmethylene to olefins is strongly influenced by steric effects in the reaction substrate, and for highly substituted olefins hydrogen abstraction is favored over addition to the π bond: M. E. Hendrick, W. J. Baron, and M. Jones, Jr., *J. Am. Chem. Soc.*, **93**, 1554 (1971).

(9) G. L. Closs, *Top. Stereochem.*, **3**, 193 (1968).

(10) G. L. Closs and B. E. Rabinow, *J. Am. Chem. Soc.*, **98**, 8190 (1976).

(11) D. Bethell, G. Stevens, and P. Tickle, *Chem. Commun.*, 792 (1970).

(12) D. Bethell, D. Whittaker, and J. D. Callister, *J. Chem. Soc.*, 2466 (1965).

(13) H. E. Zimmerman and D. H. Paskovich, *J. Am. Chem. Soc.*, **86**, 2149 (1964); H. M. Frey and R. Walsh, *Chem. Commun.*, 158 (1969); T. A. Baer and C. D. Gutsche, *J. Am. Chem. Soc.*, **93**, 5180 (1971).

(14) W. J. Baron, M. E. Hendrick, and M. Jones, Jr., *J. Am. Chem. Soc.*, **95**, 6286 (1973).

(15) In general one does *not* know the ratio of stereoisomers formed from cyclization of a trimethylene diradical, but in the case of PhCHCH₂CHD the *cis*:*trans* ratio for the cyclopropanes formed must be very near to unity and hence a ratio of carbene spin states undergoing addition can be estimated on the assumption that the singlet undergoes addition with complete stereospecificity, and that the biradical intermediate in the addition of the triplet carbene lives long enough to attain equilibrium between conformations leading to *cis* and *trans* cyclopropanes.

(16) D. Bethell, J. Hayes, and A. R. Newall, *J. Chem. Soc., Perkin Trans. 2*, 1307 (1974).

Table I. Product Yields from Photolysis of Diphenyldiazomethane in Mixtures of 1,2-Dichloroethylenes and Hexafluorobenzene

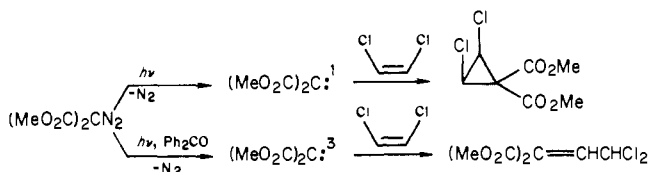
reactants			product yields, % (absolute)		stereospecificity of cyclopropanation, % dominant stereoisomer	yield ratio (Ph ₂ C=CHCHCl ₂ × 100)/(Ph ₂ C=CHCHCl ₂ + 1,2-dichloro-3,3-diphenylcyclopropane)
mol % olefin	mol % C ₆ F ₆	initial concn (C ₆ H ₅) ₂ CN ₂ , mol L ⁻¹	Ph ₂ C=CHCHCl ₂	1,2-dichloro-3,3-diphenylcyclopropane		
100 cis	0	0.10	6.4	7.6	94 cis	46
60 cis	40	0.05	6.9	9.1	94 cis	43
40 cis	60	0.03	7.7	8.0	93 cis	51
26.4 cis	73.6	0.02	8.2	8.8	92 cis	48
100 trans	0	0.05	36	9	95 trans	80
100 trans	0	0.10	31.9 ± 2.6	8.4 ± 0.9	95 trans	79 ± 9
60 trans	40	0.05	34	12	93 trans	74
60 trans	40	0.05	32.3 ± 2.9	9.1 ± 1.3	95 trans	78 ± 5
40 trans	60	0.05	34	10	93 trans	77
40 trans	60	0.029	35.6 ± 2.1	9.3 ± 0.7	95 trans	79 ± 5
26 trans	74	0.018	14.6 ± 1.2	4.5 ± 0.5	94 trans	76 ± 8

would produce a product different from that formed from the singlet carbene.

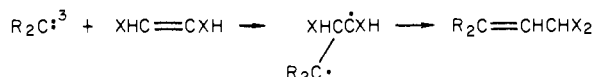
Recently several unsaturated substrates have been found whose reactions with triplet carbenes give biradical intermediates that undergo rearrangement in competition with cyclization to cyclopropanes.^{14,17-19} Two have been allowed to react with diphenylmethylene^{14,18} (Scheme III).

Neither of these substrates is suited for quantitative estimation of the proportion of singlet and triplet carbenes undergoing reaction. The terminal acetylenes give no product clearly attributable to the singlet carbene, while the yield of the product from dicyclopolyethylene clearly attributable to the triplet carbene varies strongly with temperature. This temperature dependence is probably due to the activation energy necessary for ring opening of a cyclopropylcarbinyl radical. Therefore only a small portion of the triplet carbene adduct with dicyclopolyethylene is converted by rearrangement to a product different from the singlet adduct. Since there is no stereochemical label, the amount of dicyclopolycyclopropane arising from triplet addition cannot be even approximately estimated.

Very recently, however, olefinic reaction substrates, 1,2-dihaloethylenes, have been discovered that are remarkable in yielding cyclopropanes from stereospecific addition of singlet carbenes, but a rearrangement product from addition of triplet carbenes.^{20,21}



This result is most easily understood if a biradical intermediate is formed by addition of the triplet carbene, and this trimethylene biradical undergoes halogen migration more rapidly than cyclization. It is known that halogen migrations are among the most rapid radical rearrangements.²²



In the cases thus far studied rearrangement of the biradical is more rapid than cyclization to a cyclopropane. A priori there

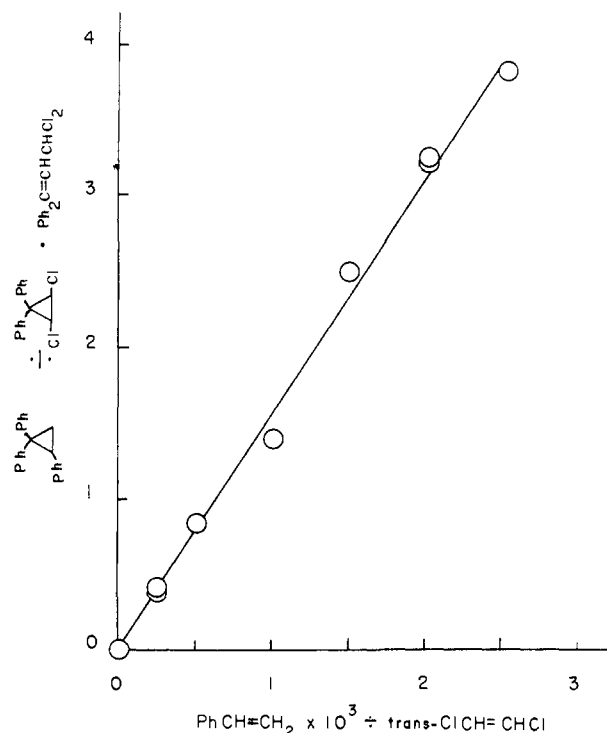
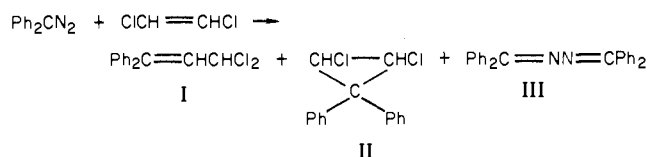


Figure 1. Product ratio from reaction of (C₆H₅)₂C: with mixtures of styrene and *trans*-1,2-dichloroethylene as a function of substrate ratio.

is no reason why cyclization should not compete with rearrangement, but this should reveal itself through the formation of a mixture of cyclopropane stereoisomers. Formation of the olefinic product may, however, provide the driving force that makes rearrangement compete favorably with cyclization.³⁰

Results and Discussion

When solutions of diphenyldiazomethane in *cis*- or *trans*-1,2-dichloroethylene are irradiated with ultraviolet light, the major products are 3,3-dichloro-1,1-diphenyl-1-propene (I), stereoisomeric 1,2-dichloro-3,3-diphenylcyclopropanes II, and benzophenone ketazine III. The yields under several reaction conditions are given in Tables I-III.



These products were identified as follows. I and III are known compounds and were compared with authentic samples. The

(17) C. S. Elliot and H. M. Frey, *Trans. Faraday Soc.*, **64**, 2352 (1968).

(18) N. Shimizu and S. Nishida, *J. Am. Chem. Soc.*, **96**, 6451 (1974).

(19) M. E. Hendrick and M. Jones, Jr., *Tetrahedron Lett.*, 4249 (1978).

(20) J. B. Lambert, K. Kobayashi, and P. H. Mueller, *Tetrahedron Lett.*, 4253 (1978).

(21) M. Jones, Jr., V. J. Tortorelli, P. P. Gaspar, and J. B. Lambert, *Tetrahedron Lett.*, 4257 (1978).

(22) J. W. Wilt in "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley, New York, 1973, p 333; W. H. Urry and J. R. Eiszner, *J. Am. Chem. Soc.*, **73**, 2977 (1951); **74**, 5822 (1952); W. H. Urry, J. R. Eiszner, and J. W. Wilt, *ibid.*, **79**, 918 (1957).

Table II. Product Yields from Photolysis of Diphenyldiazomethane in Mixtures of *trans*-1,2-Dichloroethylene and Styrene

reactants		product yields, % (absolute)			stereospecificity of cyclopropanation, % dominant stereoisomer	yield ratio $(\text{Ph}_2\text{C}=\text{CHCHCl}_2 \times 100)/(\text{Ph}_2\text{C}=\text{CHCHCl}_2 + 1,2\text{-dichloro-3,3-diphenylcyclopropane})$
mol % styrene	initial concn $(\text{C}_6\text{H}_5)_2\text{CN}_2$, mol L ⁻¹	$\text{Ph}_2\text{C}=\text{CHCHCl}_2$	1,2-dichloro-3,3-diphenylcyclopropane	1,2,2-triphenylcyclopropane		
0	0.026	36	9	0	96% <i>trans</i>	80
0.25	0.021	20.0	6.2	10.3	95% <i>trans</i>	76
0.25	0.016	17.8	6.1	9.9	<i>a</i>	74
0.50	0.016	28	8.5	30	<i>a</i>	77
1.0	0.016	22.5	7	41	<i>a</i>	76
1.5	0.021	10.2	3.3	33.6	95% <i>trans</i>	76
2.0	0.016	8.5	3.0	37	<i>a</i>	74
2.0	0.021	10.7	3.8	47	95% <i>trans</i>	74
2.5	0.016	6.8	2.6	35.8	<i>a</i>	72

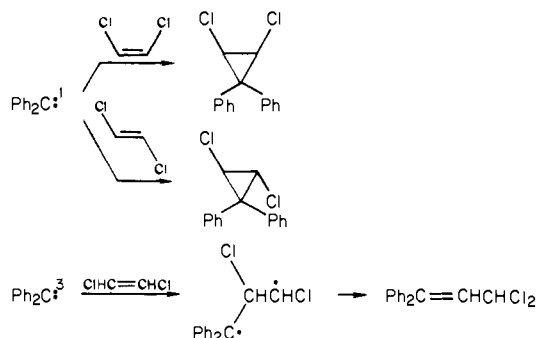
^a Not determined.Table III. Product Yields from Photolysis of Diphenyldiazomethane in Mixtures of *trans*-1,2-Dichloroethylene and Isobutylene

reactants		product yields, % (absolute)			stereospecificity of cyclopropanation, % dominant stereoisomer	yield ratios × 100	
mol % isobutylene	initial concn $(\text{C}_6\text{H}_5)_2\text{CN}_2$, mol L ⁻¹	$\text{Ph}_2\text{C}=\text{CHCHCl}_2$	1,2-dichloro-3,3-diphenylcyclopropane	1,1-dimethyl-2,2-diphenylcyclopropane		$\text{Ph}_2\text{C}=\text{CHCHCl}_2 / (\text{Ph}_2\text{C}=\text{CHCHCl}_2 + 1,2\text{-dichloro-3,3-diphenylcyclopropane})$	1,1-dimethyl-2,2-diphenylcyclopropane / $(\text{Ph}_2\text{C}=\text{CHCHCl}_2 + 1,2\text{-dichloro-3,3-diphenylcyclopropane})$
15	0.02	33.8 ± 2.4	9.4 ± 0.9	6.8 ± 0.5	95% <i>trans</i>	78 ± 5	16 ± 1
30	0.02	18.7 ± 1.9	6.2 ± 0.7	10.4 ± 0.5	94% <i>trans</i>	75 ± 11	42 ± 4

structure of II was assigned on the basis of ¹H and ¹³C NMR spectroscopy in addition to elemental analysis.

Care was taken to demonstrate that the products are *not* from a dark reaction, and thus they can be attributed to diphenylmethylene. It was shown that I and II are stable under the irradiation conditions and thus both are primary reaction products.

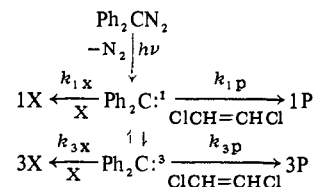
The high degree of stereospecificity observed is in accord with a reaction scheme in which cyclopropane II comes almost entirely from addition of singlet diphenylmethylene, while the triplet carbene is the source of the propylene I formed by rearrangement of a diradical intermediate. It is agreed that concerted addition requires a singlet carbene. It has been argued that singlet carbenes need not undergo concerted addition, but that conformational equilibration in a diradical will be rapid.²³ Hence the observation of stereospecific addition implies the reaction of a singlet carbene. Addition with rearrangement requires a diradical intermediate, which it is reasonable, in this case, to believe is derived from the triplet carbene.²⁴



The small amount of nonstereospecific addition is presumably due to cyclization as a minor pathway for the diradical intermediate.

The results of Table I reveal that the ratio of rearrangement product I to cyclopropanes II differs for the *cis*- and *trans*-di-

chloroethylenes, but the degree of stereospecificity of cyclopropane formation is not appreciably altered. This implies that the ratio of singlet to triplet carbenes that react with the olefin varies from one geometrical isomer to the other. One explanation for this observation is an equilibrium between singlet and triplet diphenylmethylene. Consider the following reaction scheme:



Here 1P represents all reaction products from singlet diphenylmethylene and dichloroethylene; 1X represents all products from reactions of singlet diphenylmethylene with adventitious scavenger or impurity X. 3P and 3X have analogous meanings.

If a singlet-triplet equilibrium is maintained during the reaction, then a different 1P:3P product ratio for the *cis*- and *trans*-dichloroethylenes can be explained as due simply to a different rate constant ratio k_{1p}/k_{3p} for the two olefins. An alternative explanation that does not invoke a singlet-triplet equilibrium is that an impurity or adventitious scavenger X (e.g., precursor diphenyldiazomethane) competes with the dichloroethylenes for both carbenes. The relative reactivity of X and dichloroethylene toward singlet and triplet diphenylethylene would then differ for the two olefin stereoisomers.

This latter reaction scenario can be shown to be improbable by experiments in which a substrate that can compete with dichloroethylene for diphenylmethylene is deliberately added to the *trans* olefin. In the presence of various amounts of styrene, the data of Table II indicate that the ratio of rearrangement product I and cyclopropane II stays constant, while their absolute yields decrease with added styrene. Figure 1 shows that the ratio of adduct yields from the mixtures of styrene and *trans*-dichloroethylene is a linear function of the substrate ratio. From the slope of this plot styrene is found to be 154 ± 13 times as reactive as *trans*-dichloroethylene toward the mixture of diphenylmethylene spin states.

If one assumes that the low relative reactivity of *trans*-dichloroethylene makes it a reasonable inert diluent, and uses Jones'

(23) P. P. Gaspar and G. S. Hammond in "Carbene Chemistry", 1st ed., W. Kirmse, Ed., Academic Press, New York, 1964, Chapter 12.

(24) In principle one spin state of the carbene could react via two mechanisms, one concerted, the other stepwise, as long as these paths lead to different products.

Table IV. Product Yields from Photolysis of Diphenyldiazomethane in Mixtures of *trans*-1,2-Dichloroethylene, Styrene, and Hexafluorobenzene

reactants ($\frac{[\text{Ph}_2\text{C}=\text{CH}_2]}{[\text{ClCH}=\text{CHCl}]}$ $\times 100$)	initial concn ($\text{C}_6\text{H}_5)_2\text{CN}_2$ mol L ⁻¹	product yields, % (absolute)			stereospecificity of cyclopropan- ation, % dominant stereoisomer	yield ratios	
		$\text{Ph}_2\text{C}=\text{CHCHCl}_2$	1,2-dichloro- 3,3-diphenyl- cyclopropane	1,2,2-triphenyl- cyclopropane		$\frac{(\text{Ph}_2\text{C}=\text{CHCHCl}_2 \times 100)}{(\text{Ph}_2\text{C}=\text{CHCHCl}_2 + \text{1,2-dichloro-3,3-diphenylcyclopropane})}$	$\frac{(\text{1,2,2-triphenyl-cyclopropane} \times 100)}{(\text{Ph}_2\text{C}=\text{CHCHCl}_2 + \text{1,2-dichloro-3,3-diphenylcyclopropane})}$
0.5	0.032	21.4 ± 0.9	6.6 ± 0.5	16.1 ± 1.1	95% trans	76 ± 6	58 ± 6
0.5	0.028	17.4 ± 2.3	6.0 ± 1.0	15.5 ± 1.8	94% trans	74 ± 7	66 ± 7
0.5	0.021	19.9 ± 2.4	5.3 ± 0.7	15.5 ± 1.7	93% trans	79 ± 9	62 ± 6
0.5	0.013	17.7 ± 1.4	4.9 ± 0.3	12.2 ± 0.8	94% trans	78 ± 6	54 ± 4

data on the stereospecificity of addition of diphenylmethylene to *cis*- β -deuteriostyrene¹⁴ to infer that 10% of the styrene adduct is from singlet and 90% from triplet diphenylmethylene, then one can work out that styrene is ca. 50 times as reactive as dichloroethylene toward singlet diphenylmethylene but 170 times as reactive toward triplet, if equilibrium is maintained between the singlet and triplet states of the carbene.

To account for the observation of a constant ratio of cyclopropane II (principally from singlet diphenylmethylene) and rearrangement product I (from triplet diphenylmethylene) from dichloroethylene in the presence of styrene *without* an equilibrium between carbene spin states one would have to postulate a selectivity between the two olefins that is exactly equal for singlet and triplet diphenylmethylene, i.e., $k_{1X}:k_{1P} = k_{3X}:k_{3P}$. But in fact, as seen above, the selectivity seems to differ for the singlet and triplet.

When isobutylene instead of styrene is allowed to complete with *trans*-1,2-dichloroethylene for diphenylmethylene, there is once again a constant ratio of II to I, as indicated by the data of Table III. Isobutylene is found to be 0.94 ± 0.07 times as reactive as *trans*-dichloroethylene toward the mixture of carbene spin states.

Another kind of experiment speaks for the establishment of a singlet-triplet carbene equilibrium for diphenylmethylene. Dilution with hexafluorobenzene of diphenyldiazomethane-dichloroethylene mixtures does not alter the ratio of the rearrangement product I attributed to triplet carbene and the stereospecifically formed cyclopropanes II believed to be the product of the singlet carbene. The data are given in Table I. Neither the absolute nor the relative yields change over the range of moderator concentrations found by Jones and Rettig to significantly alter the stereospecificity of addition of fluorenylidene to *cis*-2-butene. Jones and co-workers had previously found that the stereospecificity of addition of diphenylmethylene to *cis*- β -deuteriostyrene is reduced by dilution with hexafluorobenzene. The present results suggest that spin-state equilibrium is established.

When hexafluorobenzene moderator is added to mixtures containing a constant ratio of styrene and *trans*-1,2-dichloroethylene, the product ratios, given in Table IV, are not altered and this again points to a completely relaxed mixture of carbene spin states.

Conclusions

The addition of diphenylmethylene to *cis*- and *trans*-1,2-dichloroethylene has been found to give the corresponding 1,2-dichloro-3,3-diphenylcyclopropane with greater than 90% stereospecificity. A product of addition with rearrangement, 3,3-dichloro-1,1-diphenyl-1-propene, is also obtained, and this is the major product from the *trans* olefin. If the argument is accepted that the rearrangement product comes entirely from triplet carbene and the cyclopropane principally from the singlet carbene, then this result is a further indication that 1,2-dichloroethylene is a useful reagent for chemically distinguishing the reactions of singlet and triplet carbenes.

Neither the ratio of cyclopropane to propylene product nor the stereospecificity of cyclopropane formation is altered by the addition of a competing olefin or by the presence of an excess of hexafluorobenzene, which acts as an inert moderator toward diphenylmethylene. These observations are in accord with the establishment of a mobile equilibrium between the lowest singlet and triplet electronic states of diphenylmethylene under the reaction conditions.

Experimental Section

General. Routine nuclear magnetic resonance (NMR) spectra were recorded on a Hitachi Perkin-Elmer R-24B instrument, while a JEOL JNM-FX100 Multinuclear 100-MHz FT spectrometer was used for characterization of previously unreported compounds. Deuteriochloroform was used as solvent in all cases, with ca. 1% Me₄Si added as an internal standard. All photolyses were carried out at 35 °C using a Hanovia medium-pressure mercury lamp shielded with uranium glass.

Yields. In most cases, reported yields are determined by NMR spectral integration relative to toluene, which is added as a quantitative standard just prior to analysis. The ¹H NMR spectra of the unidentified

products consist primarily of aromatic resonances. Benzophenone ketazine is formed in all cases.

Preparation of Diphenyldiazomethane (DPDM). The diphenylcarbene precursor was prepared by the yellow mercuric oxide oxidation of benzophenone hydrazone and purified by recrystallization from petroleum ether.²⁵

Purification of *trans*-Dichloroethylene. *trans*-Dichloroethylene (Aldrich) was purified by fractional distillation using a 2-ft vacuum-jacketed column packed with glass helices, bp 48–49 °C.

Purification of *cis*-Dichloroethylene.²⁶ Commercially available *cis*-dichloroethylene contains ca. 20% chloroform, which is an efficient triplet-carbene scavenger and difficult to separate using conventional techniques. To obtain chloroform-free *cis*-dichloroethylene, a solution of 20 g of bromine in 500 g of *trans*-dichloroethylene was irradiated under N₂ in a quartz photolysis well with Rayonet low-pressure mercury lamps for 6 h. The solution was then run through an alumina column and distilled on the above fractionating column, giving 140 g of *cis*-dichloroethylene, bp 60–61 °C, containing less than 0.5% chloroform and 1% *trans* isomer.

Irradiation of DPDM in *trans*- or *cis*-Dichloroethylene. In a typical experiment, 100 mg of DPDM in 5 mL of dichloroethylene was degassed in three freeze-pump-thaw cycles, sealed in a Pyrex ampule, and irradiated for 2 h. After removal of the solvent by vacuum distillation, the crude reaction mixture was examined by NMR spectroscopy. On a larger scale (1 g in 150 mL) the irradiation was done under N₂ using a quartz immersion well. Results were similar in both cases. Cyclopropane adduct was isolated by chromatography on a 15 × 400 mm silica gel column using 1:10 chloroform-hexane and recrystallized from cyclohexane, mp 130–131 (*trans* adduct II) or 123–126 °C (*cis* adduct II). 3,3-Dichloro-1,1-diphenyl-1-propene (I) underwent hydrolysis to the corresponding aldehyde during the chromatography. *trans*-Cyclopropane (II): ¹H NMR δ 3.99 (s, 2 H, cyclopropyl ring protons) and 7.35 (m, 10 H, phenyl); ¹³C NMR 29.6 (Ph₂C-), 43.8 (-CHCl), 127.4, 128.5, and 137.7 (phenyl) ppm; mass spectrum *m/e* 227 (parent -Cl). The ¹³C satellites in ¹H gave *J*_{C,H1} = 191.5 and *J*_{trans}(H-H_{vic}) = 3.2 Hz. *cis*-Cyclopropane (II): ¹H NMR δ 3.82 (s, 2 H, cyclopropyl ring protons) and 7.17–7.42 (m, 10 H, phenyl); ¹³C NMR 38.99 (Ph₂C-), 42.74 (-CHCl), 126.33, 127.21, 127.55, 128.28, 128.91, 131.30, 135.44, and 143.39 ppm (phenyl). The ¹³C satellites in ¹H NMR gave *J*_{C,H1} = 191.2 and *J*_{cis}(H-H_{vic}) = 6.8 Hz. Anal. Calcd for C₁₅H₁₂Cl₂: C, 68.46; H, 4.59; Cl, 26.94. Found (*trans* II): C, 67.82; H, 4.65; Cl, 27.52. (*cis* II): C, 67.88; H, 4.73; Cl, 27.41.

Irradiation of DPDM in Dichloroethylene and Hexafluorobenzene. Varying amounts of hexafluorobenzene were added to 100 mg of DPDM and 5 mL of *cis*- or *trans*-dichloroethylene in Pyrex ampules and irradiated as above.

Irradiation of DPDM in Styrene. DPDM (100 mg) in 10 mL of styrene was irradiated in a Pyrex ampule as above. Excess styrene was removed by vacuum distillation and the crude mixture analyzed by NMR. The only product was identified as 1,1,2-triphenylcyclopropane:²⁷ ¹H NMR δ 1.67, 1.88, and 2.76 (q, 3 H, ABX pattern of cyclopropyl ring protons) and 6.6–7.2 (m, 15 H, phenyl).

Irradiation of DPDM in *trans*-Dichloroethylene and Styrene. DPDM (100 mg) was added to 32 mL of *trans*-dichloroethylene solutions containing 0.25–2.5 mol % styrene in Pyrex ampules and irradiated as above. Control experiments with shielded ampules containing the same solutions resulted in no formation of 1,1,2-triphenylcyclopropane.

Irradiation of DPDM in *trans*-Dichloroethylene, Styrene, and Hexafluorobenzene. Varying amounts of hexafluorobenzene were added to 100 mg of DPDM in 16 mL of a *trans*-dichloroethylene solution containing 0.5% styrene and irradiated as before in a Pyrex ampule.

Irradiation of DPDM in *trans*-Dichloroethylene and Isobutylene. DPDM (100 mg) was added to 30 mL of *trans*-dichloroethylene solutions containing 15 and 30 mol % isobutylene in Pyrex ampules and irradiated as before. Excess reactants were removed by vacuum distillation and the crude mixture was analyzed by NMR. In addition to the *trans*-dichloroethylene adducts, 1,1-dimethyl-2,2-diphenylcyclopropane¹⁴ was found: ¹H NMR δ 1.00 (s, 6 H, Me's), 1.14 (s, 2 H, cyclopropyl ring protons), and 6.7–7.3 (m, 10 H, phenyl).

Preparation of 3,3-Diphenyl-3-hydroxy-1-propyne.²⁸ Liquid ammonia (500 mL) was condensed into a 1-L, three-necked, round-bottom flask equipped with a mechanical stirrer and a dry ice condenser. Acetylene gas was bubbled through at a fast rate and 9.5 g of sodium was added in small portions to this solution. After the solution had turned gray-white (~1 h), 60 g of benzophenone in 127 mL of anhydrous ether was added dropwise through an addition funnel (2 h). After the mixture was stirred for 6 h, condenser cooling was discontinued and the liquid NH₃ permitted to evaporate overnight. Ice water was cautiously added to the reaction flask. The mixture was acidified with dilute H₂SO₄ and extracted three times with ether. The ether layers were washed with a saturated NaCl solution, then dried over anhydrous MgSO₄. After removal of the solvent, 59.5 g of a yellow oil remained, which solidified overnight in the refrigerator.

Preparation of 3,3-Dichloro-1,1-diphenyl-1-propene (I).²⁹ The above propyne (6.0 g) was dissolved in 60 mL of anhydrous ether in a 250-mL three-necked flask equipped with a gas bubbler, magnetic stirrer, and addition funnel while HCl gas was slowly bubbled through this solution; a solution of 12 g of PCl₃ in 30 mL of anhydrous ether was added dropwise (45 min) while stirring. The solution was stirred for an additional 2 h, then cautiously poured over 250 mL of ice. After melting, the mixture was neutralized with aqueous NaOH, then extracted three times with ether. The ether layer was washed two times with H₂O, then dried over anhydrous MgSO₄. After removal of the ether, a yellow oil remained which was shown by NMR analysis to consist of 78% of the desired propene. ¹H NMR: δ 6.05 and 6.33 (2 H, AB quartet, *J* = 12 Hz) and 6.9–7.4 (m, 10 H, phenyl).

Photochemical Stability of the Cyclopropanes and Rearranged Product. *trans*-1,2-Dichloro-3,3-diphenylcyclopropane (II, 75 mg) and 3,3-dichloro-1,1-diphenyl-1-propene (I) were each dissolved in 4 mL of *trans*-dichloroethylene in Pyrex ampules, degassed, sealed, and photolyzed for 2 h. After removal of solvent, no change was noted in their NMR spectra.

Acknowledgments. This work has been supported by the National Science Foundation under Research Grant CHE-75-20163.

(25) L. I. Smith and K. L. Howard, "Organic Syntheses", Collect. Vol. III, Wiley, New York, 1955, p 351.

(26) W. Schroth and J. Peschel, *Chimia*, **18**, 171 (1964).

(27) A. Sonoda, I. Moritani, S. Yasuda, and T. Wada, *Tetrahedron*, **26**, 3075 (1970).

(28) D. Papa, F. J. Villani, and H. F. Ginsberg, *J. Am. Chem. Soc.*, **76**, 4446 (1954).

(29) H. Doupeux and J. Simonet, *Bull. Soc. Chim. Fr.*, 1219 (1972).

(30) This suggestion was made by referee and is acknowledged with gratitude.