

THE PHOTSENSITIZED DECOMPOSITION OF METHYL DIAZOMALONATE (1)

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(Received 29 December 1966; in revised form 10 February 1967)

CONVENTION dictates that triplet carbenes be ascribed radical-like properties. This view is based on inadequate knowledge of triplets in solution and on data from the gas-phase reactions of methylene. The former cases are largely confined to the phenyl-substituted carbenes and are notable both for their scarcity and lack of compass. One must not minimize the important contributions of Rabinovitch (2), Bader (3), Frey (4), and others (5) but a detailed understanding of the properties of methylene in the gas-phase is just beginning to emerge from a most complicated picture.

The whole question is further clouded when it is realized that in only two cases have both spin states of a given carbene been observed in solution. As has been wisely warned (6) for a high degree of certainty to be attached to a claim of determination of spin state in a reaction, both must be observed. Neither our previous work on fluorenylidene (7,8) nor Hammond's on methylene (9) presents a detailed description of the properties of both spin states. In the former case the properties of singlet fluorenylidene are obscured by ready intersystem crossing to the more stable (10) triplet, in the latter the process of photosensitization apparently does not produce triplet methylene cleanly.

We have previously (11) reported the direct photolysis of methyl diazomalonate (I) and indicated that the benzophenone-photosensitized (12) decomposition produced a different species. Here is a new case in which the two spin states may be compared. It is expected that triplet bis-carbomethoxy-carbene (II) will be formed by loss of nitrogen from triplet I formed in turn by energy transfer from triplet benzophenone.

The most marked change in going from the direct photolysis to the sensitized is in the stereochemistry of the cyclopropanes produced by the addition of the carbene to cis- and trans-olefins. The direct photolysis (11) of I yields a species which adds to cis-4-methyl-2-pentene to give 92% cis-cyclopropane(III) and only 8% trans(IV). By contrast, (table 1) the sensitized decomposition gives ca. 88% trans-cyclopropane starting from either cis- or trans- olefin.

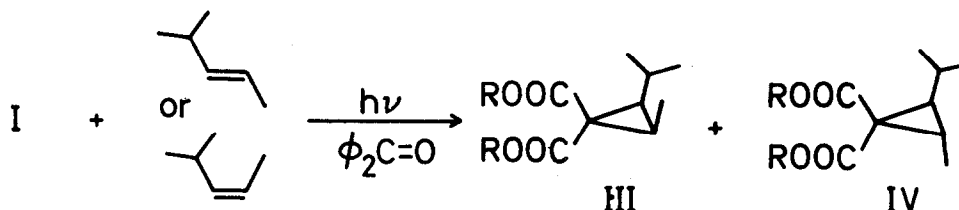
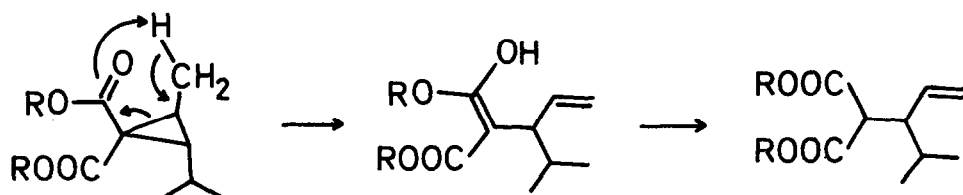


TABLE 1

<u>Conditions</u>	<u>%III</u>	<u>%IV</u>	<u>Yield</u>
I + <u>cis</u> -4-methyl-2-pentene	92	8	39.8
I + <u>trans</u> -4-methyl-2-pentene	10	90	24.3
I + Ph_2CO + <u>cis</u> -4-methyl-2-pentene	10	90	43.0
I + Ph_2CO + <u>trans</u> -4-methyl-2-pentene	14	86	--

Appropriate control experiments were performed. Under the reaction conditions there is insignificant isomerization of the solvent and the products are neither isomerized nor destroyed. The familiar mechanism is proposed in which triplet II adds to the olefin to give a diradical in which rotation about a carbon-carbon single bond competes with spin inversion and closure. One would expect, if rotation prevailed sufficiently over closure, that the thermodynamic ratio of the two cyclopropanes might be approached from either olefin. Indeed, in this case both cis- and trans-olefin lead to very similar mixtures of cyclopropanes. An attempt to determine the thermodynamic ratio of III and IV failed as a thermal rearrangement, akin to those discovered by McGreer (13) and Roberts (14) intervened.

A further property of carbenes is their ability to discriminate between olefins. In general, singlets appear to be electrophilic species, although the bulkier carbenes are sensitive to steric factors (11). Only fragmentary data are available for triplets. It has been reported (15) that diphenylcarbene, presumably reacting as a triplet, adds to butadiene and 1,1-diphenylethylene



one-hundred times faster than to cis-2-butene. This comparison is unsatisfactory as diphenylcarbene reacts with cis-2-butene primarily by hydrogen abstraction (16), not addition. Triplet fluorenylidene has been shown to react faster with butadiene than cis-4-methyl-2-pentene (8), but no quantitative data are yet available. Skell (17) has reported that triplet 2,3-dimethylcyclopropylidene reacts 20 times faster with butadiene than with trans-2-butene. Table 2 compares the relative rates of addition of singlet and triplet bis-carbomethoxycarbene to several olefins.

TABLE 2

<u>Olefin</u>	<u>Singlet II</u>	<u>Triplet II</u>
2,3-dimethyl-butene-2-	.88	.33
2-methyl-2-butene	1.0	1.0
1-pentene	.47	.46
3,3-dimethyl-1-butene	.48	.48
<u>cis</u> -4-methyl-2-pentene	.55	.15
<u>trans</u> -4-methyl-2-pentene	.23	.13
2,3-dimethyl-1,3-butadiene	1.3	4.4
1,3-butadiene	-	4.5

Our data correlate reasonably well with the limited examples available. The factor of 42 in going from trans-4-methyl-2-pentene to butadiene is comparable to Skell's factor of 20 for a similar change (17). It is clear that dramatic changes in rate occur when the olefin is a diene. The rationalization proposed by Skell suffices to explain the change. The diradical formed by triplet addition to the diene is resonance stabilized. No such stabilization is available to the singlet which effectively adds in a single step.

It has often been alleged that triplet carbenes do not insert in the

carbon-hydrogen bond (18-20). This is by no means a settled question and Rabino-
vitch (21) has recently postulated just such a process. The problem is an espe-
cially difficult one as a triplet might be expected to abstract hydrogen to give
two radicals which could recombine to give apparent insertion product. We can-
not settle this question but our data do show that triplet insertion is no more
than a minor process in solution.

A change from direct to sensitized decomposition of I in cyclohexane re-
sults in a drop in yield of cyclohexylmalonic ester from 32% to 8%. Similarly,
while direct irradiation of I in 2,3-dimethylbutane led to insertion products
in 46% yield, the sensitized decomposition gave only 13%. In place of insertion
product two new compounds, dimethyl malonate and 1,1,2,2-tetracarboxymethoxyethane
appeared (table 3).

TABLE 3

<u>Conditions</u>	<u>Insertion</u>	<u>CH₂R₂</u>	<u>R₂CH-CHR₂</u>
I + 2,3-dimethylbutane	46	trace	trace
I + 2,3-dimethylbutane + Ph ₂ CO	13	23	38

The data fit a scheme in which triplet II abstracts hydrogen to give two radi-
cals which give products by recombination, dimerization or further hydrogen ab-
straction. It seems very likely that most if not all the "insertion product"
is created by recombination of radicals.

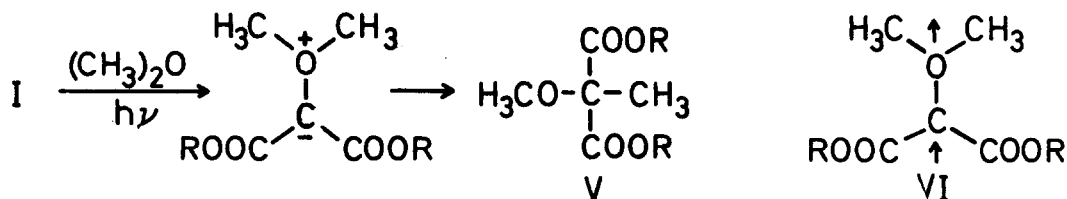
There is a small change in the ratio of the hydrogens attacked by singlet
and triplet II (table 4). The triplet appears to be slightly more selective
than the singlet, but not remarkably so.

TABLE 4

<u>Hydrocarbon</u>	<u>Ratio</u>	<u>Singlet II</u>	<u>Triplet II</u>
2,3-dimethylbutane	3/1	13.1(12.5) ²²	20
n-pentane	2/1	3.4	5.1
n-butane	2/1	4.7(8.4) ²²	6.6

We have only begun to look for new reactions of triplets but it seems ap-
propriate to mention one non-reaction. Numerous examples are known of the re-
action of carboxy-carbenes with the carbon-oxygen bond (23). The generally

Accepted mechanism involves the formation of an ylid which subsequently decomposes to product. Bis-carbomethoxycarbene is no exception as V can be isolated



from the irradiation of I in dimethyl ether. However the sensitized decomposition produces no V. Apparently complexes of the type VI are either not formed or do not rearrange to product.

Convention seems vindicated. The properties associated with triplet carbenes, usually summarized as "radical-like character," and predicted largely on an intuitive basis, are correct. One problem remains. Carbene chemistry in general has long been plagued by the difficulty of differentiating reactions of excited diazo compounds from those of carbenes. It can be legitimately argued, as it has by a referee, that our (and previous⁹) data require only a species different from that produced in the direct irradiation. An alternative to triplet carbene is triplet diazo compound (I).

We have only fragmentary data bearing on this point and report it here only in most preliminary form. If excited diazo compound were strongly involved in these reactions addition of hexafluorobenzene, an inert medium, should allow the intermediate to live long enough so that nitrogen can be lost to give the triplet carbene. Such additions produce only very small changes in the properties reported above, and the rate of decomposition of I is unaffected. Should triplet diazo compound and triplet carbene share very similar properties this result would be fortuitous. While we do not think this likely, it is not impossible and more definitive experiments are in progress.

REFERENCES AND NOTES

1. We thank the National Science Foundation for support of this work in the form of NSF-GP-5257 and two National Science Foundation Undergraduate Participation Fellowships to A. K. Jr. We also thank the Lilly Research Laboratories for a generous unrestricted grant.
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