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PHOTOSENSITIZED DECOMPOSITION OF 1-PHENYLDIAZOETHANE. SPIN MULTIPLICITIES OF CARBENES IN THE HYDROGEN MIGRATION

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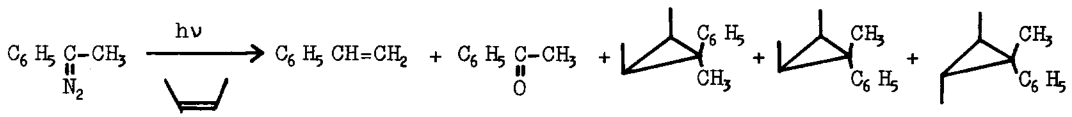
It has been demonstrated in the preceding letter that the rate of hydrogen migration exceeds that of the phenyl in the reaction of benzylcarbene and the hydrogen migration might presumably occur only in the singlet carbene$^{1)}$. The present paper aims to report additional results on the spin multiplicities of carbenes in the hydrogen migration.

Photochemical decomposition of 1-phenyldiazoethane (I) in *cis*- or *trans*-2-butene resulted in the formations of styrene (II), acetophenone (III), and cyclopropanes (IV, V, and VI) as shown in the Table I. The stereochemical structures of the cyclopropane derivatives were determined by means of nmr spectroscopy$^{2)}$.



(I) (II) (III) (IV) (V) (VI)

It is to be noted that the addition of phenylmethylcarbene to olefins is found to be non-stereospecific but it is not complete; similar mixtures of the isomeric cyclopropanes were obtained in the decompositions of I in two different olefins, but much more *cis*-cyclopropanes were produced in the reaction of I with

Table I. Direct and Photosensitized Decomposition of I

Solvent	$C_6H_5COC_6H_5$ (Concn)[b]	Products (%) II	III	IV+V+VI	VI/(IV+V)	V/IV
trans-2-Butene[a]	0	7.0	2.0	7.0	91/9	0.5
cis-2-Butene[a]	0	6.0	2.3	6.9	4/96	1.2
cis-2-Butene[a]	0.36	3.7	20.2	7.1	8/92	0.8
cis-2-Butene[a]	1.33	1.7	45.9	6.0	15/85	0.8
Diethylether	0	30.5	13.4			
Diethylether	0.36	13.4	28.4			
Diethylether	1.33	7.8	35.4			

a) Solutions of 0.04 mole/l of I in 800ml of butene and 200ml of ether were irradiated for 40 min using a high pressure Hg lamp. b) Mole/l

cis-olefin and much more *trans*-cyclopropane with trans-olefin. This might be argued that both singlet and triplet carbene are the reactive species in the reaction3). It is also notable that II is formed in appreciable amounts in these reactions, indicating that the hydrogen migration is in competition with the addition reaction. Thus the present reaction provides a useful tool to investigate the spin multiplicities of carbenes in the hydrogen migration; one can increase the amounts of triplet species either by a photosensitization4) or by a dilution technique3) and study both stereospecificities of the addition reaction and degrees of the hydrogen migration from the yields of II under such conditions.

A photosensitized decomposition of I was carried out in the present experiments because this might give triplet carbene directly4) and hence least complicated*. The experimental results are summarized in the Table I. It was

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* The dilution technique might produce the singlet carbene at first and it might have a certain life time before it converted to the triplet by the collisional deactivation3). In this technique there will be possible contaminances of the reactions of singlet carbene, thus the hydrogen migration might suffer this kind of complications.

confirmed in control experiments that there were observed no isomerizations of the olefins and the products under the reaction condition.

Since both IV and V have cis-configuration, the stereospecificities of the addition must be evaluated by the VI/IV+V. When benzophenone was absent in the reaction system, the figure for the addition of phenylmethylcarbene to cis-2-butene was 4/96, while it increased up to 15/85 in the presence of sensitizer. Apparently, the increase** of the photosensitizer in its amount resulted in the depression of stereospecificities in the addition reaction; this is attributable to the increased amounts of the triplet species. The fact that the amounts of III increased in the presence of sensitizer is also consistent with the increased triplet carbenes[5)]. The combined yields of the addition products remained rather constant under these conditions***.

Now, the yields of styrene under these conditions deserve our attention. In the presence of photosensitizer, the yield dropped from 6.0 to 1.7% and the same was also true for the simple decomposition of I in diethylether; from 30.5 to 7.8%****. These results are consistent with the assumption that the hydrogen migration occurs in the singlet carbene and the triplet does not play a role in the migration.

** The amounts of benzophenone used in present experiments were larger than those used in other experiments[4)]. When the irradiating light is selected so as to excite specifically the sensitizer, the small amounts of sensitizer[4)] are effective enough to bring about the completely photosensitized decomposition. In the present case, however, filtration was not applied for the light source and hence the non-sensitized photolysis of I competed with the photosensitized decomposition. Accordingly, the larger amounts of sensitizer were needed to bring about the appreciable amounts of triplet species in the present experiment.

*** Yields of the cyclopropanes were low in all cases, but spin multiplicities of the carbene could safely be concluded from the stereochemical results of the addition reaction. This has also be discussed in several instances[6)].

**** That the decrease of the yield of II were not due to the succeeding secondary reactions caused by the addition of benzophenone was confirmed by a control experiment; after II was irradiated in the presence of benzophenone under the same condition as above, the unchanged II was recovered in 96% yield.

Recently, Zimmerman7) and Jones8) have reported the rearrangements in the carbenic reactions and shown that phenyl or alkyl migrations have taken place in singlet carbenes. Jones and Ando8) have proposed an explanation that a large energy difference between the singlet state and the triplet of the reaction product is an important factor for facile rearrangement in singlet carbenes. However, rates of the reaction depend upon the energy difference between the ground state and the transition state and not necessarily depend upon the energy difference of the final states. Accordingly, we prefer to taken a following explanation. The migration to a vacant *p*-orbital of the singlet carbene is similar to those observed in the numbers of carbonium ion reactions and hence it is facile, but the migration to an odd electron containing orbital of the triplet carbene might not be favorable, because it is a kind of radical rearrangements which are scarecely observed in the organic reactions9)

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