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DIRECT AND SENSITIZED PHOTODECOMPOSITIONS OF 1-PHENYLDIAZOETHANE

THE SPIN STATE IN THE 1,2-HYDROGEN MIGRATION TO THE CARBENE CENTER

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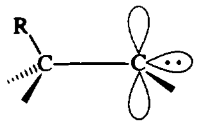
Abstract—Direct and sensitised photodecompositions of 1-phenyl-diazoethane (**2**) were investigated in *cis* and *trans*-2-butenes, and also in ethyl ether. In *cis*-2-butene photosensitisation led to the increased formation of acetophenone (**5**) and to loss of stereospecificity of the addition reaction. In ethyl ether an increased yield of **5** was obtained. On the other hand, the yield of styrene (**4**), which was produced via 1,2-hydrogen migration, decreased with sensitisation. These results indicate that the spin state in the 1,2-hydrogen migration to the divalent carbon is singlet.

INTRODUCTION

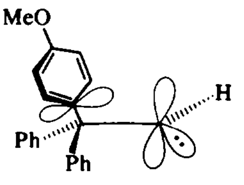
The reactions of carbenes may for convenience be divided into four categories; addition, insertion, abstraction, and rearrangement.[1,2] While the addition reaction has been the subject of much discussion,[1,2] our interest has centered on the fourth type of reaction, especially 1,2-hydrogen migration to a divalent carbon.[3–7] The following information is now available on the migration reaction; (i) spin state,[3,4,8–11] (ii) stereochemistry,[6,10–13] and (iii) solvent effect.[5,7,14]

Concerning the first topic (i), in 1967 Kirmse and Buschhoff investigated the effect of substituents on the intramolecular reaction of aliphatic carbenes.[11] They proposed I for 1,2-alkyl group migration to a carbene center, in which the R group migrates to a vacant p-orbital.



I

In 1968, Zimmerman and Munch demonstrated that the anisyl migratory aptitude in the thermal decomposition of 2-anisyl-2,2-diphenyldiazoethane was larger than unity.[8] This led them to propose that the anisyl group migrated with bonding to an electron deficient orbital, as in II.

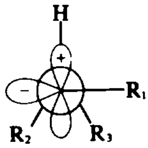


II

Although these proposals suggest intervention of singlet carbene in the 1,2-migration reactions, both authors failed to produce evidence that the aryl[8] or alkyl[11] migration to the divalent carbon proceeded through the singlet state. In 1968, we presented preliminary evidence that the spin state of the divalent carbon in the 1,2-hydrogen migration reaction of 1-phenyldiazoethane is singlet.[3]

Almost at the same time, Jones and Ando reported that singlet carbenes are involved in the Wolff rearrangement of diazoketones.[15] Based upon the results on the reaction of a C atom with carbonyl compounds[16] and unsaturated hydrocarbons,[17] Skell *et al* supported our conclusion. More recently, Sohn and Jones, elaborating on our work,[3] reported that the 1,2-hydrogen migration reaction of methyldiazopropionate also proceeds through singlet carbene.[9]

Secondly, on the stereochemistry of 1,2-hydrogen migration, we previously reported that this could be well interpreted by the Newman projection (III) of a singlet carbene, and is controlled by steric and electronic factors of the substituents.[6] The stereochemistry of olefins derived from β-alkoxycarbenes,[11] α,β-dicarboalkoxycarbene,[6] alkylcarbenes,[6] α,β-diphenylethylidene,[6] and β-thiocarbenes[12] was successfully explained with the aid of III. More recently, some elegant work has been presented by Nickon *et al.*[13] They indicated that the ease of 1,2-hydrogen migration depends upon the geometry of the carbene, the perpendicular orientation being better than the antiplanar one. This conclusion was in accordance with our initial proposal (III).



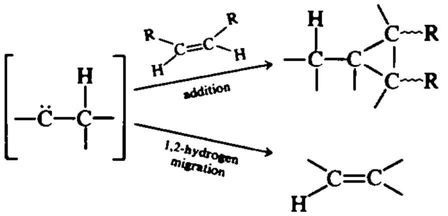
III

Finally, topic (iii), solvent effect on 1,2-hydrogen migration, was investigated both by our[5,7] and Liu's groups.[7,14] There are two possible types of solvent effect; the effect on the stereochemistry of olefins produced via 1,2-hydrogen migration,[14] and the effect on the intermediates involved in the migration reaction of diazo compounds.[5,7] The former problem can be successfully explained by III.[14] The later problem, whether the real intermediate was a carbonium ion and/or a carbene, was not straightforward, high sensitivity to solvent being shown.[5 7]

In this paper we report in full on the spin state of the divalent carbon in the 1,2-hydrogen migration.

RESULTS AND DISCUSSION

In order to investigate the spin state of 1,2-hydrogen migration, it was necessary to select an appropriate reaction system. The addition of carbenes to olefins, leading to cyclopropanes, has been studied in great detail, and the relationship between the spin state and the stereochemistry of cyclopropanes is well established.[1,2] Therefore, it appeared that a carbene in which both addition and hydrogen migration occur concurrently was desirable for such investigation (eqn 1), since we can know the spin state of the carbene from the addition reaction, and can connect the spin with the 1,2-hydrogen migration.



(1)

Generally speaking, alkyl carbenes are prone to undergo 1,2-hydrogen migration, but only with difficulty add to olefins. On the other hand, aryl carbenes more easily undergo the addition than the migration reaction.[1,2]

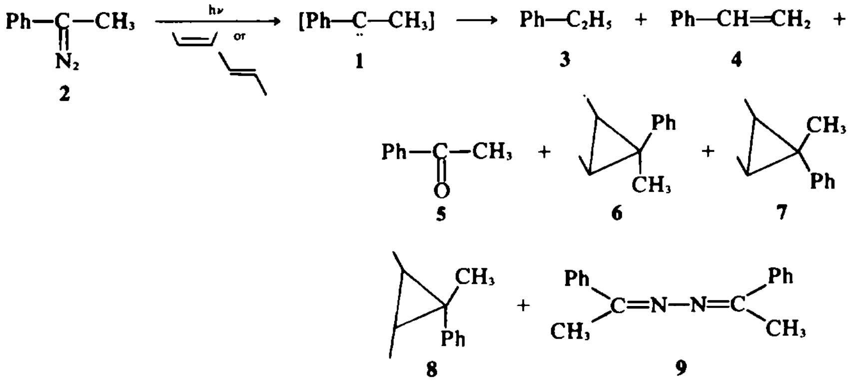
It was anticipated that phenylmethylcarbene (1) would meet our purpose, and in fact it had been reported by Overberger and Anselme* that 1 gave styrene via 1,2-hydrogen shift.[18] Moreover, Closs and Coyle had indicated that the photochemical reaction of 1-phenyldiazoethane (2) with *cis*-2-butene produced cyclopropanes along with styrene.[19] Consequently, we chose to examine 1, as a target which would be characteristic of both alkyl and aryl carbenes.

Direct photolysis in cis *and* trans-2-*butenes*. Direct photodecomposition of 2 was carried out in *cis* and *trans*-2-butenes with a high pressure Hg lamp. After nitrogen evolution ceased, the reaction products were distilled under vacuum. The volatile products were analysed by gas chromatography. It was found that the residue, which crystallized on standing, was acetophenone azine (9). The results are summarized in Table 1 and eqn (2).

Ethylbenzene (3) is produced via hydrogen abstraction by 1 from the solvent, butene and/or ether. Reaction of 1 with oxygen dissolved in the solvent gives acetophenone (5). Carbene (1) also affords the 1,2-hydrogen migration product (4) and the addition products (6, 7 and 8). There are two possibilities for the origin of 9; dimerization of 2 and/or reaction of 1 with 2.[18] The former seems to be favorable in the thermal decomposition of 2.[18] However, this problem is not important for the final conclusion.

The major difference between the reaction in *trans*-2-butene and that in *cis*-isomer was the stereochemistry of cyclopropanes (6, 7 and 8). From *trans*-2-butene, *trans*-2,3-dimethyl-1-methyl-1-phenylcyclopropane (8) was obtained as the main addition product, together with the *cis*-isomers (91% *trans*, 9% *cis*). On the other hand, from *cis*-2-butene, *cis*-2,3-dimethylcyclopropane derivatives (6 and 7) were predominantly formed, along with the *trans*-isomer (96% *cis*, 4% *trans*). This ratio was somewhat variable; in benzene-*cis*-2-butene solvent the ratio changed to 94% *cis* and 6% *trans*. These results, namely nonstereospecific addition, suggested that triplet phenylmethylcarbene (1) was involved in the reaction.

Here, it may be worth while to mention the difference between our result and previous data.[19] Closs and Coyle



(2)

Table 1. Decompositions of 2 in olefins[a]

Olefin	$Ph_2C{=}O$ (mole)	Products (%)[b] 3	4	5	6+7+8	8/6+7	7/6
trans-2-Butene	0	0·5	7·0	2·0	7·0	91/9	0·5
cis-2-Butene	0	0·6	6·0	2·3	6·9	4/96(6/94)[c]	1·2
cis-2-Butene	0·36	0·6	3·7	20·2	7·1	8/92	0·8
cis-2-Butene	1·33	0·3	1·7	45·9	6·0	15/85	0·8

[a] Solutions of 36 mmol of 2 in 800 ml of butene and 200 ml of ether were irradiated unless otherwise indicated. [b] By GLPC analysis of the volatile products. [c] Benzene was used instead of ethyl ether.

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*They assumed that the singlet carbene must be involved in the formation of styrene, though they gave no evidence for this.

obtained only *cis*-cyclopropanes (**6** and **7**) from the reaction in *cis*-2-butene, and they made no mention of formation of the trans-isomer (**8**). This result seems to suggest a spereospecific addition. Moreover, their yield of cyclopropanes was higher than ours. These differences may be due to the reaction temperature; the photolysis in our case was carried out at 5° while their's was at −40°. In fact, stereospecificity increases at lower temperature in the photolysis of diphenyldiazomethane.[20]

The present nonstereospecificity is of relatively small degree. If a triplet state is reacting without intervention of a singlet state, nearly complete stereochemical scrambling should be observed. For example, carbenes such as methylene,[21,22] fluorenylidene,[23] diphenylmethylene,[20,24] carboalkoxycarbenes,[25] ketocarbenes,[15,26,27] and dicyanocarbene[28] show a higher degree of nonstereospecificity in their triplet states. Consequently, it appears that the present low degree of nonstereospecificity can be ascribed to mixing of both the singlet and triplet states. It is reasonable to assume that the singlet state adds to the olefins stereospecifically and the triplet state nonstereospecifically, and that the carbene (**1**) exists largely in the singlet state. If so, one can increase the amount of the triplet either by photosensitization[15,22,25,26] or by a dilution technique.[27,28]

Photosensitized decomposition in cis-2-*butene.* Accordingly, photosensitized decomposition of **2** was carried out in the presence of benzophenone and *cis*-2-butene. The results are summarized in Table 1. It was confirmed by control experiments that isomerization of neither the olefin nor the products occurred under the reaction conditions.

As is apparent from Table 1, the ratio of *trans* to *cis*-cyclopropanes, **8**/**6** + **7**, increases up to 15/85 in the presence of a large excess of benzophenone. Obviously, the photosensitization causes substantial, but not complete, loss of stereospecificity. This indicates that sensitization increases the proportion of triplet species, as would be expected.

Another remarkable change is that the yield of **5** increases from 2·3 to 45·9%. It is well known that oxygen reacts preferentially with a triplet rather than a singlet carbene.[1,2,29] Therefore, this result also demonstrates increase of the triplet species. Trace amounts of **3**, presumably the origin of which is the triplet species,[1,2] are produced regardless of the decomposition method. The yields are rather constant; 0·3–0·6%. The ratio of **7**/**6** changes slightly with sensitization, but the reason for this is not clear.

The changes in stereochemistry and yield of the cyclopropanes are relatively slight. It may be argued that photosensitization should induce increased formation of a cyclopropane[9] and also induce considerable stereochemical scrambling.[15,25,26] However, triplet phenylmethylcarbene must react predominantly with oxygen instead of *cis*-2-butene.

It should be mentioned that the amounts of benzophenone were somewhat larger than those used in previous experiments.[22,25,26] When the irradiating light is selected so as to specifically excite the sensitizer, small amounts of sensitizer are sufficiently effective to bring about completely photosensitized decomposition. Absorptions at 250 and 520 mμ were observed for **2**. Hardly any decomposition of **2** was induced by irradiation at near 520 mμ, but decomposition was rapid at near 250 mμ. Benzophenone shows a UV absorption at 253 mμ;[30] therefore, under irradiation from a high pressure Hg lamp there would be competition of sensitized decomposition with non-sensitized photolysis. Consequently, large amounts of the sensitizer were necessary to generate the triplet state effectively.

The yields of styrene (**4**) deserve our attention. On photosensitization, the yield dropped from 6 to 1·7%. It was confirmed by a control experiment that the decrease was not due to succeeding reactions possibly caused by the addition of benzophenone. Consequently, this result indicates that 1,2-hydrogen migration becomes more difficult as the amount of triplet species increases.

Direct and sensitized decomposition in ether. The change of yield of **4** on sensitization in *cis*-2-butene was relatively slight, and it seemed necessary to demonstrate a more dramatic change if further discussion based on the yield were to be made. We reasoned that if the decomposition were carried out without the olefin, the addition reaction would be avoided and a more marked increase in the formation of **4** would result. Fortunately, this was the case. The direct and sensitised decompositions were performed in ethyl ether. The results are summarized in Table 2.

Table 2. Decomposition of **2** in ethyl ether[a]

$Ph_2C{=}O$ (*mole*)	Product (%)[b] **3**	**4**	**5**
0	2·4	30·5	13·4
0·23	2·9	13·4	28·4
0·85	1·6	7·8	35·4

[a] Solution of 23 mmol of **2** in 400 ml of ethyl ether was irradiated.

[b] By GLPC analysis of the volatile products.

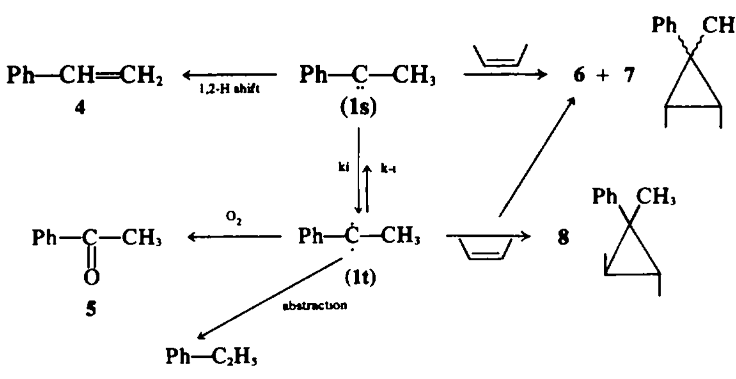
The change in yield of **3** is not smooth. However, the yield of **5** increases with photosensitisation in the same way as in the above experiment. Contrarily, the yield of **4** decreases dramatically from 30·5 to 7·8%. Consequently, here also, the result indicates that 1,2-hydrogen migration is reduced by generation of the triplet state.

CONCLUSION

The results are all consistent with the mechanism shown in Scheme 1. It is clear that there is an equilibrium between singlet and triplet diphenylcarbene.[20] Accordingly, it is reasonable to suppose such an equilibrium for the related phenyl carbene (**1**). Since electron spin resonance shows a triplet ground state for **1**,[31] the rate of intersystem crossing from singlet to triplet, ki, must be larger than the rate of inverse intersystem crossing, k-i.

Direct photolysis produces first the signlet (**1s**) which gives styrene (**4**) and cyclopropanes (**6** + **7**). The equilibrium allows intervention of the triplet (**1t**), as the minor component, which affords ethylbenzene (**3**), acetophenone (**5**), and cyclopropanes (**8** and small amounts of the *cis*-isomers).

On photosensitization, the situation is reversed; **1t** is formed as the major component, with **1s** being present mainly owing to equilibrium. The major reaction of **1t** is with oxygen instead of the olefin, which leads to the increased formation of **5**. The small degree of nonstereospecificity indicates that the cyclopropanes are largely



Scheme 1.

produced via **1s**. Suppression of the formation of **4** on sensitization is due to the decreased formation of **1s**.

In conclusion, the 1,2-hydrogen migration proceeds via the singlet state. The migration to the vacant p-orbital of the singlet carbene is anlogous to that observed in numerous carbonium ion reactions, and hence it is facile. The migration to the odd electron containing orbital of the triplet carbene mimics a radical 1,2-rearrangement, a reaction scarcely observed in organic chemistry.[32]

EXPERIMENTAL

All temps. are uncorrected. IR spectra were recorded with a Hitachi-S2 spectrophotometer. NMR spectra were obtained with a Japan Electron Optics JNM-4H-100 spectrometer. Chemical shifts are given in δ-scale, ppm downfield from TMS as internal standard, with splitting patterns and relative integrated area. UV spectra were measured with a Hitachi EPS-2U spectrometer. VPC analyses were carried out on a Yanagimoto 5DH using a 5·25 m × 0·3 cm column packed with 10% Apiezon L on firebrick.

Materials. 1-Phenyldiazoethane (**2**) was prepared according to the method previously described.[33] The ether soln of **2** was titrated with benzoic acid. The concentration of the soln was determined from the amount of N_2 evolved. The olefins (>99·9% pure) were commercially available, and the other solvents and benzophenone were purified by standard techniques.

Direct photolysis in olefin. A soln of 36 mmol of **2** in 800 ml of the olefin and 200 ml of ethyl ether (or benzene) was irradiated at *ca.* 5° using an Eikosha high pressure Hg lamp. Evolution of N_2 ceased within 40 min. The solvents were evaporated at atmospheric pressure. The ppt was removed by filtration and washed twice with ether. The combined mother liquor was distilled under 4 mm Hg at a bath temp of *ca.* 150°. The distallate and the materials collected in the dry-ice trap were analysed by GLPC. The residue, which crystallised on standing, and the ppts were recrystallized individually from EtOH. Both substances melted at 120–121°, indicating them both to be (**9**); lit. m.p. 120–121°C.[34] The yields of the volatile products were determined by GLPC and are based upon **2**. Authentic samples of **3**, **4** and **5** are commercially available.

1-Phenyl-1-methyl-2,3-dimethylcyclopropanes (**6**, **7** and **8**). These products were distilled from the mixture and purified by GLPC; b.p. 62–67°/5 mm Hg. The structures were mainly determined from the NMR spectra, which were same with reported data;[19] **6**, NMR (in CCl_4) 0·89 (broad s, 8H), 1·27 (s, 3H), 7·19 (s, 5H); (Found: C, 90·07; H, 9·97. Calcd. for $C_{12}H_{16}$: C, 89·94; H, 10·06%); **7**, NMR (in CCl_4) 1·07 (broad s, 8H), 1·19 (s, 3H), 7·24 (s, 5H); (Found: C, 89·94; H, 10·04%); **8**, NMR (in CCl_4) 1·0–0·3 (m, 2H), 0·70 (d, 3H), 1·20 (d, 3H), 1·31 (s, 3H), 7·16 (s, 5H); IR (neat) 1603, 1490, 1445, 765, 703 cm^{-1} (This IR spectra were almost identical with those of **6** and **7**.); (Found: C, 90·20; H, 10·13%).

Sensitized photolysis in olefin. A soln of 36 mmole of **2** and benzophenone (65·6 or 242 g) in 800 ml of the olefin and 200 ml of ethyl ether was irradiated as above. Benzophenone was recovered in essentially quantitative yield.

Direct and sensitized photolysis in ethyl ether. A soln of 23 mmol of **2** in 400 ml of ethyl ether was irradiated. Sensitised decomposition was carried out with a solution of **2** (23 mmole) and benzophenone (42 g or 155·6 g) in ether (400 ml). The analytical procedure was the same as above. Benzophenone was again recovered in essentially quantitative yield.

Control experiments

(a) *Check for isomerization of the olefin.* The olefin recovered after irradiation in *cis*-2-butene and benzophenone was checked by GLPC. No isomerization could be detected.

(b) *Check for isomerization of the adducts.* A soln of 58 mg of **6** and 650 mg of benzophenone in 20 ml of ether was irradiated for 1 hr. GLPC analysis revealed no isomerization to **7** or **8**. The same experiment with **7** also showed no isomerization.

(c) *Check for decrease in amount of* **4**. A soln of styrene (1·04 g, 10 mmole) and benzophenone (32·8 g, 180 mmole) in ether (100 ml) and *cis*-2-butene (400 ml) was irradiated for 1 hr. GLPC analysis revealed that **4** was recovered in essentially quantitative yield.

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