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A ROUTE TO 4,5-DIAZAFLUORENYLIDENE: PREPARATION, PHOTO- AND THERMAL REACTIONS OF 9-DIAZO-4,5-DIAZAFLUORENE

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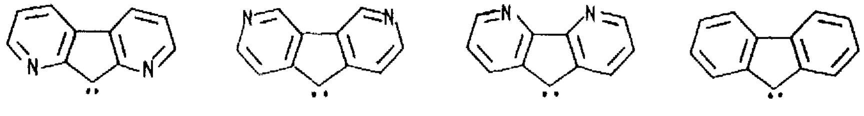
Summary: 9-Diazo-4,5-diazafluorene(5), a novel carbene precursor was prepared and irradiated in the presence of methanol, mono- and diolefins. The carbene 3 has been found to react primarily from its singlet state.

The chemistry of diarylcarbenes as well as fluorenylidene belongs to the class of carbenes equilibrating between singlet and triplet state. They have been the subject of many investigations.[1] Type and position of the heteroatoms affect the physical as well as chemical properties of the carbene under study. In continuation to our interest in carbene chemistry and related to Schuster's[2,3] work on 1,8-and 3,6-diazafluorenylidene (1,2),the third isomer 4,5-diazafluorenylidene (3) was the subject of the present study to throw light on the differences of spin states as well as chemical reactivities of these isomers (1,2,3) compared with the parent fluorenylidene (4). The novel precursor of 3, 9-diazo-4,5-diazafluorene was prepared starting with 1,10-phenanthrolene according to the literature procedure with some modifications for related compounds.[4-6]

Scheme 1

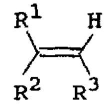


1 2 3 4

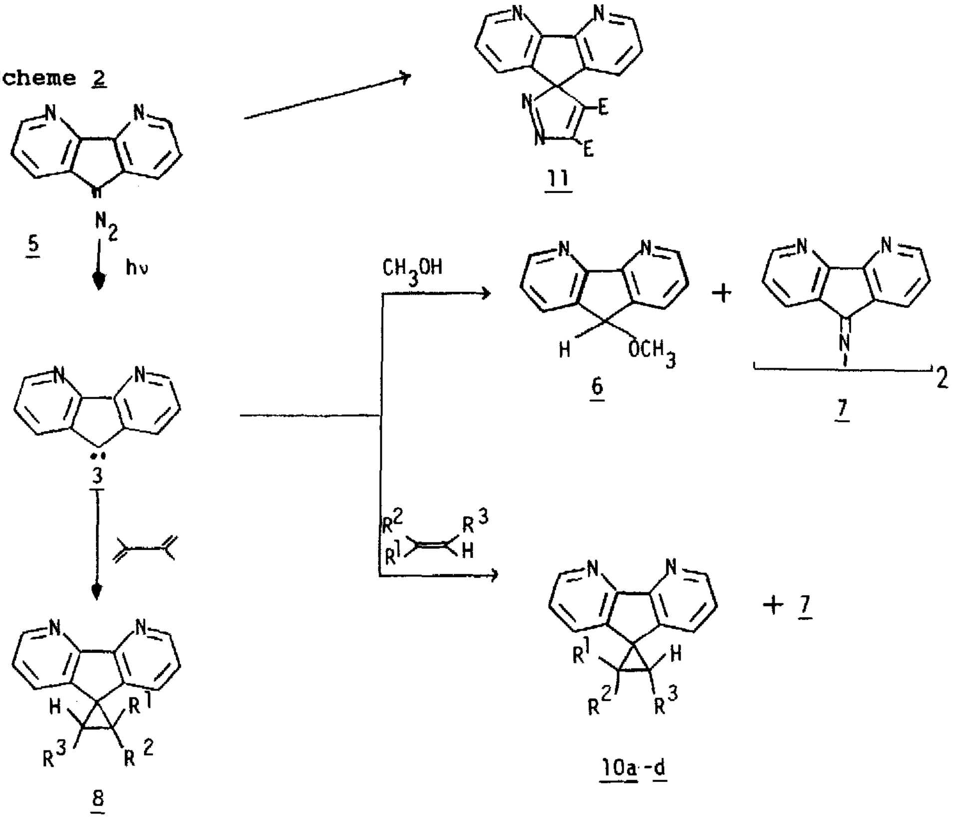
Irradiation of 5 in methanol, styrene, p-methylstyrene, -methylstyrene, trans-ß-methylstyrene or in 2,3-dimethyl-1,3-butadiene gave in contrast to the results of Schuster[2,3], no detectable diazirine intermediate. In methanol, the irradiation products are a mixture of ether (6, 26%), as insertion product of the singlet of 3, in addition to the ketazine of 4,5-diazafluorene (7, 18%). The ketazine was observed in all preparative experiments. Schuster reported on the formation of 7 only with 2. 7 was the sole product upon irradiation of 3 in 2,3-dimethylbutene. However,irradiation of 4 in 2,3-dimethyl-1,3-butadiene gave the spiro compund 8. Furthermore, trapping of 3 in styrene, p-methylstyrene, p-methoxystyrene and α-methylstyrene (9a-c) afforded the corresponding spirocyclopropane derivatives (10a-c) only. The structures of 10a-c were confirmed by elemental analysis MS, ^{1}H-NMR, ^{13}C-NMR spectroscopy.

Now it is obvious that direct irradiation of 5 gave products indicative of the generation of carbene 3. In each of the aforementioned reactions, this carbene undergoes reactions characteristic of the singlet state. To prove the spin state of 3 more clearly, photolysis of 5 was carried out in pure (>99,5%) trans-ß-methylstyrene 9d and the reaction mixture was separated by column chromatography (SiO_2, ethyl acetate/methanol). Only one isomer was obtained and was shown to be the trans-ß-methylstyrene adduct 10d. No evidence for the formation of the cis-adduct 10e was found.
Stereospecifity is usually considered as evidence that the reactive state in the cyclopropanation is the singlet of the carbene.[7,8]

Table

Olefins: 	R^1	R^2	R^3	Products	Yield(%)
styrene	C_6H_5	H	H	10a	33
p-methylstyrene	CH_3-C_6H_4	H	H	10b	38
trans-ß-methylstyrene	CH_3	H	C_6H_5	10d	25
α-methylstyrene	CH_3	C_6H_5	H	10c	54
2,3-dimethyl-1,3-butadiene	H	C_3H_5	H	8	25
2,3-dimethyl-2-butene				7	23

Scheme 2



Irradiation of 5 in trans-ß-methylstyrene in the presence of benzophenone as a triplet sensitizer, does not change the type of product ratio. An accepted explanation for this observation is that the ground triplet state reacts indirectly via the thermally accessible singlet state[9,10], indicating that the rate (k_s) of the irreversible bimolecular reaction of the singlet carbene is high.

Scheme 3

$$3\ (\uparrow\uparrow) \underset{k_{st}}{\overset{k_{ts}}{\rightleftarrows}} 3\ (\uparrow\downarrow) \xrightarrow{k_s} \text{Singlet product}$$

Furthermore, the reaction of 5 with acetylene dicarboxylate gave the corresponding pyrazole derivative (11, 30%) through 1,3-dipolar addition.

A full study of the chemistry of carbene 3 is currently in progress in this laboratory.

Acknowledgement:

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**) Paper 24 on cycloalkene-carbenes. Paper 23 see: ref. 9c.

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