4,5-Diazafluorenylidene: Preparation, Reactivity, Multiplicity, and Selectivity Studies[☆]

Abdel-Magd A. Abdel-Wahab^a, Mohamed T. Ismail^a, Omima S. Mohamed^a, Heinz Dürr*^b, and Yinmin Ma^c

Chemistry Department, Faculty of Science, Assiut University^a, Assiut, Egypt

Fachrichtung 11.2, Organische Chemie der Universität des Saarlandes^b, D-66041 Saarbrücken, Germany Fax: (internat.) +49(0)681/302-4105 E-mail: hd@rz.uni-sb.de

Chemistry Department of Northwest University^c, Xian, 710069, China

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The chemistry of 4,5-diazafluorenylidene (3), generated from the diazo compound **3a** by photolysis, has been studied with regard to reactivity, multiplicity and selectivity. Reaction of **3** in 2,3-dimethylbutene gave exclusively ketazine **24**. The [1 + 2] cycloaddition with styrenes **5**-**11** afforded cyclopropanes **16**-**23** in 25-54% yields and **24** as a side product. In these reactions no diazirine intermediate was involved. Irradiation of **3a** in methanol afforded the ether **26** (25% yield). The stereoselectivity of **3** was studied by its addition to (*E*)- and (*Z*)- β -methylstyrene. A mixture of the (*E*)- and (*Z*)-cyclopropanes **22** and **23**, respectively, was detected. Thus for **3**, tri-

Electronic effects, through bond or through space, play an important role in various properties of molecules. These effects are most sensitively felt in carbenes^[1-3]. Due to the small energy gap between singlet and triplet only small changes are observed in these species 1–3. Electron-withdrawing atoms such as N in 1,8-Fl (1), and 3,6-Fl (2), were shown to favour the triplet ground state of diarylcarbenes^[4,5]. Donating groups, on the other hand, gave singlet ground states for the carbenes **A** and **B** (Scheme 1). Fluorenylidene **C** is clearly a triplet species.

Schuster's fine work^[4,5a,b] showed the effect of *o*- or *p*-N on the carbene center (I and M effects) (vide infra). We studied **3**, where N is in the *m* position, and therefore should only exhibit inductive effects (-I) on the carbene center. Differences between **3** and 1,8- and 3,6-Fl should then shed more light on the efficiency of -I and -M effects on carbene multiplicity and reactivity. On the other hand **3** can be regarded as vinylogue of Arduengo's carbenes $4^{[6a-c]}$. Arduengo et al. have recently been able to prepare the long-sought first stable carbenes and their structure has been established by X-ray analysis.

1. Reaction of 4,5-Diazafluorenylidene (3)

The novel precursor of 3, 9-diazo-4,5-diazafluorene (3a), was prepared from 1,10-phenanthrolene, according to literature procedure with some modifications for related com-

plet multiplicity was concluded. The results of competition experiments with singlet/triplet scavengers (methanol/dimethylbutadiene) demonstrated that an equilibrium between singlet and triplet manifold of **3** exists at room temperature. Selectivity studies with carbene **3** were carried out by evaluating the competition experiments of the cycloaddition of **3** with differently substituted styrenes. A plot of the $k_{\rm rel}$ values from the competition studies versus Hammett σ constants gave $\rho = -0.65$ indicating that carbene **3** reacts as an electrophile.

Scheme 1



pounds^[7]. The diazo-group absorption is clear from the IR spectrum of **3a** as a sharp peak at 2080 cm⁻¹. Diazo compound **3a** was irradiated in different trapping agents such as styrene (**5**), *p*-methylstyrene (**6**), *p*-methoxystyrene (**7**), *p*-chlorostyrene (**8**), *p*-nitrostyrene (**9**), α -methylstyrene (**10**)

and trans- β -methylstyrene (11) in addition to 2,3-dimethyl-2-butene (12), 2,3-dimethyl-1,3-butadiene (13), methanol (14) and benzene (15) (Scheme 2). The photolysis was monitored by TLC and the products were separated using different chromatographic procedures, mainly column chromatogaphy, and the results are compiled in Table 1.

Scheme 2



The results revealed that irradiation of **3a** in styrenes **5–11** gave no detectable diazirine intermediates in contrast to the findings of Schuster^[4,5a]. The corresponding spirocyclopropane derivatives **16–23** were obtained together with the ketazine of 4,5-diazofluorenone **24** in trace to low yields. The structures of **16–23** were confirmed by elemental analysis, mass spectroscopy, and ¹H- and ¹³C-NMR spectroscopy. For example, the mass spectrum of compound **16** revealed a molecular ion peak, representing also the base peak, at m/z = 270.12 corresponding to C₁₉H₁₄N₂. The NMR spectrum of **20** displayed the characteristics of

Table 1. Photolysis of 9-diazo-4,5-diazafluorene (3a) in different
trapping agents 5-15

Entry	Trapping agents	Time [min]	Products (yield %)
1	Styrene (5)	3	16 (33), 24 (20)
2	<i>p</i> -Methylstyrene (6)	5	17 (38), 24 (3)
3	p-Methoxystyrene (7)	4	18 (40), 24 (trace)
4	<i>p</i> -Chlorostyrene (8)	6	19 (35), 24 (6)
5	p-Nitrostyrene (9)	6	20 (39), 24 (trace)
6	α -Methylstyrene (10)	6	21 (54), 24 (3)
7	(E) - β -Methylstyrene (11a)	7	22 (25), 24 (5)
8	(Z) - β -Methylstyrene (11b)	13	22, 23 (68) ratio 1:3
9	2,3-Dimethyl-2-butene (12)	16	24 (24)
10	2,3-Dimethyl-		
	1,3-butadiene (13)	4.5	25 (24), 23 (9)
11	Methanol (14)	3	26 (25), 23 (18)
12	Methanol (14)	0.5	26 (5), 3a (69), 24 (trace)
13	Benzene (15)	4	27 (44), 24 (7)

cyclopropane ring protons of an ABX spectrum. Extending the scale between $\delta = 2$ and 4 revealed the splitting of the H signal into a triplet (double doublet) [$\delta = 3.47$ (t/dd, ${}^{3}J_{ca}$ $= {}^{3}J_{cb} = 6.67$ Hz, 1H, H_c)] and H_a and H_b into two double doublets [$\delta = 2.43$ (dd, ${}^{3}J_{bc} = 6.67$ Hz, ${}^{2}J_{ba} = 8.44$ Hz, 1H, H_b), 2.36 (dd, ${}^{3}J_{ac} = 6.67$ Hz, ${}^{2}J_{ab} = 8.44$ Hz, 1H, H_a)].

The presence of electron-withdrawing atoms in the ring (nitrogen atom) deshielded the *ortho* and *para* protons, the *meta* protons are also deshielded but to a smaller extent. The ¹³C-NMR spectrum of compound **16** showed signals of three aliphatic carbon atoms at $\delta = 21.15$, 32.04, and 34.24. Using ¹³C-DEPT technique^[8] the three peaks are ascribed to the cyclopropane ring carbon atoms, viz., the peaks at $\delta = 21.15$ for C-3', at $\delta = 32.04$ for C-1' and that at $\delta = 34.24$ for C-2'. Compilation of information gathered from the spectral data (vide supra) and the results of elemental analysis confirmed the structure for **16**. Similar spectral data confirming the structure were obtained for **17**, **18** and **19**. The ¹H-NMR and ¹³C-NMR data for the spirocyclopropanes **16–23** are shown in Table 4.

Furthermore, the ketazine 24 was observed in all preparative experiments and rigorously identified by elemental analysis and spectroscopy. Its formation is due to a bimolecular reaction between the diazo compound with the carbene^[9]. Schuster reported on the formation of ketazine with only 3,6-diazafluorenylidene (2). Surprisingly, ketazine 24 was the sole product upon irradiation of 3a in 2,3-dimethylbut-2-ene (12). Perhaps the addition of this carbene at the hindered double bond is difficult or impossible under these reaction conditions.

It has been found that 2,2-diphenylcyclopropylidene adds to tetramethylethylene in low yield only and this was attributed to steric hindrance between the carbene's phenyl substituents and olefinic alkyl groups^[10]. However, irradiation of **3a** in 2,3-dimethyl-1,3-butadiene (**13**), a typical reaction for triplet carbenes^[11], gave in addition to **24** the spiro compound **25**. The ¹H- and ¹³C-NMR spectra of **25** support the proposed structure.

It is generally accepted that a carbene generated in the presence of alcohols inserts into the O-H bond to give ethers rather than into the C-H bonds of the alcohol^[12]. Accordingly, the detection of the ether in an alcoholic reac-

tion system in which carbene seems to be involved could be considered as strong evidence for the intervention of a carbene intermediate. Also, it has been proposed that O-H insertion is the characteristic reaction of singlet carbenes^[4].

Irradiation of 3a in methanol gave a mixture of the ether 26 (25%) as insertion product of the singlet form of 3, in addition to the ketazine 24 (18%). Also, photolysis of 3a in methanol for short periods gave no other products than 24 and 26, indicating that no diazirine intermediate was formed during the reaction course and that the ether is a primary product^[13]. Irradiation of 3a in benzene afforded $27 \leftrightarrow 27'$ and 24.

2. Stereoselectivity of 4,5-Diazafluorenylidene (3)

Generally, carbenes add to (Z)- or (E)-olefins to form cyclopropanes in two different ways, stereospecifically with retention of the original stereochemistry of the olefin, or nonstereospecifically with loss of the original stereochemistry of the olefin. This fact was recognized very early by Skell^[14] for the [1 + 2] cycloaddition of a carbene to an olefin.

It became clear that direct irradiation of 3a gave products indicative of the generation of carbene 3. In each of the reactions mentioned, this carbene can undergo reactions characteristic of the singlet or triplet state. To study the spin state of 3 in more detail, photolysis of 3a was carried out in pure (>99.5%) (E)- β -methylstyrene (11a) and (Z)- β methylstyrene (11b). The reaction mixtures were separated very carefully by column chromatography. Stereochemistry was assigned from the ¹H-NMR spectrum of (E)-22, which shows proton signals at $\delta = 1.61$ (d, ${}^{3}J_{Me} = 6.30$ Hz, 3H, CH₃) and the expected cyclopropane at $\delta = 3.31$ (d, ${}^{3}J =$ 7.93 Hz, 1H, H_c), 2.55 (dq, ${}^{3}J = 7.93$ Hz, ${}^{3}J = 6.30$ Hz, 1H, H_a), and of (Z)-23 at $\delta = 1.39$ (d, ${}^{3}J_{Me} = 6.6$ Hz, 3H, CH₃), 3.54 (d, ${}^{3}J = 9.5$ Hz; 1H, H_c), 2.50 (1H, H_a). The ¹³C-NMR spectrum of (E)-22 is consistent with the structure as well. The addition of 3a to the (E)-olefin 11a afforded only (E)-22, whereas 3a and the (Z)-olefin 11b gave a mixture of (Z)-22 and (E)-23. The nonstereospecificity is usually considered as evidence that the [1 + 2] cycloaddition occurs via the triplet configuration of the carbene^[14-16]. It is clear that 4,5-diaza-fluorenylidene 3 reacts via a triplet configuration. Triplet-sensitized photoreactions of diazo compounds are commonly used to bypass the singlet intermediate and to give directly a triplet carbene $\overline{1}^{17-19}$. Irradiation of **3a** in **11a** in the presence of benzophenone, as triplet sensitizer, gives only a slight change in the ratio of (E)-22/(Z)-23.

3. Competitive Quenching Experiments

To measure the singlet versus triplet reactivity of carbene **3** the change of the ratio of cyclopropane (c_{cyc}) and ether (c_{Et}) formed during photolysis of **3a** in variable mixtures of methanol and 2,3-dimethyl-1,3-butadiene was determined. Methanol has been chosen in this work as the singlet scavenger based on previous reports that alcohols react efficiently and selectively with the singlet state by an insertion

Scheme 3



reaction, but the triplet state will react only slowly by an H abstraction reaction^[3,12,20].

Also, 2,3-dimethyl-1,3-butadiene was selected as the triplet scavenger because dienes have been shown to be efficient triplet carbene traps, presumably because of the stabilization of the initially formed triplet 1,3-biradical^[3].

The ratio of ether **26** and spirocyclopropane **25** has been found to be dependent on the molar concentration of methanol and the diene in the reaction mixtures. ¹H-NMR spectroscopy was used for analysis of the photolysates. The signal of methyl groups at $\delta = 3.10$ of ether **26** and that of methyl groups at $\delta = 1.25$ or 1.56 of the cyclopropane **25** were used as reference peaks for the determination of **26** and **25**, respectively, in the reaction mixtures. The results are shown in Table 2 and represented in Figures 1A–D.

Table 2. Competitive quenching experiments: photolysis of **3a** in a mixture of methanol/2,3-dimethyl-1,3-butadiene^[a]

Entry	Diene ml $\times 10^{-2}$ M ml			Methanol $\times 10^{-2}$ M	^c Diene ^c MeOH M-% M-%		c _{cycl.} ³ Φ	c _{Et} ¹Φ	c _{cycl.} %	c _{Et} %
1	4	3.54	16	39.60	8.2	91.79	6.0	5.8	50.80	49.15
2	8	7.07	12	29.70	19.2	80.77	7.5	2.8	72.50	27.18
3	12	8.84	10	24.75	26.3	73.68	16.5	5.0	76.74	23.26
4	14	12.39	6	14.81	45.6	54.45	13.5	1.9	86.72	12.34
5	16	14.10	4	9.00	86.0	38.96	19.4	2.0	90.65	9.35

^[a] $c_{\text{cycl.}} = \text{concentration of } 24$ in the reaction mixtures; $c_{\text{Et}} = \text{concentration of } 25$ in the reaction mixtures; $c_{\text{Diene}} (\%) = \frac{[c_{\text{Diene}}]}{[c_{\text{Diene}} + c_{\text{MeOH}}]} \times 100$; $c_{\text{MeOH}} (\%) = \frac{[c_{\text{MeOH}}]}{[c_{\text{Diene}} + c_{\text{MeOH}}]} \times 100$; $c_{\text{cycl.}} (\%) = \frac{[24]}{[24-25]} \times 100$; $c_{\text{Et}} (\%) = \frac{[25]}{[24-25]} \times 100$.

It is clear from Figure 1A-D, that the reaction mixtures consist of ether 26 and spirocyclopropane 25. The percentage of each is dependent on the concentration of methanol and diene and it is evident that the slight increase in the diene concentration results in a large increase in the concentration of the cyclopropane products, at the expense of the ether formation. These findings indicate that the singlet and triplet spin states of carbene 3 are probably in equilibrium under these conditions or as a mixture of spin states and each can react in the presence of its efficient scavenger.

4. Selectivity of 4,5-Diazafluorenylidene (3)

Carbene selectivity can be determined using the Moss approach to determine $k_{\rm rel}$ for the addition to different olefin mixtures^[21]. To investigate the selectivity of carbene 3 the

Figure 1. Competitive quenching of 4,5-diazafluorenylidene (3) in a mixture of 2,3-dimethyl-1,3-butadiene (13) and methanol (14); A: relationship between $c_{\text{cycl.}}$ [%] and c_{Diene} [%]; B: relationship between c_{Et} [%] and c_{MeOH} [%]; C: relationship between ${}^{1}\phi/{}^{3}\phi$ and c_{MeOH} [mol/l]; D: relationship between ${}^{3}\phi/{}^{1}\phi$ and c_{Diene} [mol/l]





Hammett method has been employed in the present investigation; we obtained a linear relationship with $\rho = -0.65$, indicating that carbene 3 behaves as an electrophilic carbene (see Figure 2). This is simply understandable on the basis of the electron-withdrawing property of the pyridine-like nitrogen atom. Schuster has suggested, without any proof, that the other isomers 1 and 2 have electrophilic character. We have used the relative addition rate constant of the carbene to aryl-substituted olefins (such as styrenes). Plotting log $k_{\rm rel}$ against the σ values (Hammett parameter)^[22] of aryl-substituted olefins gives the equation:

$$\log k_{\rm rel} = \sigma \cdot \rho$$

where ρ is the reaction constant (Table 3).

5. 1,3-Dipolar Cycloaddition

The diazo compound 3a (9-diazo-4,5-diazafluorene) was added to dimethyl acetylenedicarboxylate to give 4,5-diazafluorene-9-spiro-3'-pyrazole-4',5'-dicarboxylate (28) at room temp. in ether/dichloromethane mixture as solvent^[23].

Discussion

A comparison of 3 (4,5-Fl) should show the significance of through-bond versus through-space transmission of elec-

p-OCH 0.25 [6] LC

Entry

1

2

3

4

ς

R

p-NO₂

p-Cl

Η

p-CH₁

$[a] k_{rel}$	$=\frac{nS}{kU};$	$\log k_{rel}$	$= \log \frac{U}{U}$	$=\log\frac{\kappa U}{kU}=\sigma$	
	 0.1			CT 73	

Table 3. Competition experiments: photolysis of **3a** in an equimolar mixture of styrene (5) and p-substituted styrenes 6-9 in ether^[a]

log k_{rel}

-0.51

-0.19

0.00

0.12

 $\sigma_{\rm p}$ values

0.78

0.23

0.00

-0.17

-0.27

15

[2]

k_{rel}

0.31

0.64

1.00

1.33

1.76

[S] = concentration of the substituted product; [U] = concentration of the unsubstituted product 16.

tronic effects with regard to Schuster's 1,8- and 3,6-Fl. This is reflected clearly in the diazo precursors. Compared to diazofluorene ($\lambda_{max} = 480$ nm) the maxima in 9-diazo-1,8diazafluorene (1) and in 9-diazo-3,6-diazafluorene (2a) $(\lambda_{max} = 413 \text{ and } 407 \text{ nm})$ are blue-shifted. 9-Diazo-4,5-diazafluorene (3a) ($\lambda_{max} = 469$ nm) shows an absorption rather close to diazofluorene. In other words electronic effects of N in the o and p position (1,8 and 3,6) of the diazo precursors are influencing the diazo bond more than in the m position (4,5). Similar effects should be present in the corresponding carbenes. The cycloaddition of 1,8-Fl (1),





3,6-Fl (2), and 4,5-Fl (3) to styrenes gives cyclopropanes. The stereochemistry in the reaction of the carbenes (1,8and 3,6-Fl) with β -deutero- α -methylstyrenes is maintained^[5]. 3 (4,5-Fl) reacts with (E)- or (Z)- β -methylstyrene with loss of stereochemistry. With 1,8- and 3,6-Fl the sensitized carbene formation, followed by cycloaddition, occurs with either complete (1,8-Fl) or partial (3,6-Fl) loss of stereochemistry. 4,5-Fl reacts under these conditions as a triplet carbene. Reactions of 1,8-, 3,6- and 4,5-Fl with benzene afford spironorcaradienes/tropylidenes. In the reaction with methanol, a typical singlet reaction, 1,8-Fl and 4,5-Fl give only the insertion product whereas 3,6-Fl affords also a dimer. Here an SET mechanism was assumed. 1,8-Fl and 3,6-Fl yield diazirines as side products. 3a forms only ketazine and no diazirine could be found in this and related reactions. The electrophilic nature of 4,5-Fl (3) was established by competition experiments. Since no such studies exist for 1,8- and 3,6-Fl (1 and 2) a comparison is not possible with these carbenes.

It has been pointed out above that carbene 3 reacts from the triplet manifold. In the competition experiments 3 and methanol/diene (variation of concentration) a singlet-triplet equilibrium or a reaction of both singlet and triplet manifold is established, and both reaction channels to singlet product 25 and triplet product 26 become available for the carbene.

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Experimental Section

General: MS MAT-311 (Varian) with electron energy 70 eV. – NMR AM 400 Aspect 3000 (Bruker), TMS as the internal standard. – UV Shimadzu double-beam Spectrophotometer UV-200 S. – Elemental analyses: "Ultramikroschnell" method according to Walisch^[24] or Elemental Analyser Mod. 1106 Carlo Erba Instrumentation. – Photolysis Systems: All photolysis reactions were carried out in a 20-ml pyrex glass cell fitted with a side arm and an internal cooling tube, and externally irradiated with a Hanovia high-pressure mercury lamp (450 W) using a pyrex filter. The whole system was set up in an aluminium container which served as a light reflector. – Materials used: 1,10-phenanthrolene (**28**), styrene (5), *p*-methylstyrene (6), *p*-methoxystyrene (7), α -methylstyrene (10), *trans*- β -methylstyrene (11) (>99.5% pure), 2,3-dimethyl-2-butene (12), 2,3-dimethyl-1,3-butadiene (13) (99.9% pure) were purchased from Aldrich Chemical Co., Ltd.; *p*-chlorostyrene (8)^[25], *p*nitrostyrene (9)^[25] and (*Z*)- β -methylstyrene (11b)^[26] were synthesized as described in the literature, and distilled before use.

1. Synthesis and Photolysis of 9-Diazo-4,5-diazafluorene (3a)

1.1 Preparation of 4,5-Diazafluorene-9-one^[6]: To a refluxing solution of 9.00 g (0.05 mol) of 1,10-phenanthrolene (**28**) and 5.00 g (0.09 mol) of potassium hydroxide in 750 ml of water, a solution of 25.30 g (0.16 mol) of potassium permanganate in 400 ml of water was added with stirring over 1 h. The product was 4,5-diazafluoren-9-one (**29**), yield 3.30 g (36%); m.p. 212°C (ref.^[19] 211°C).

1.2 Preparation of 4,5-Diazafluorenone Hydrazone^[7]: A mixture of 5.00 g $(2.75 \times 10^{-2} \text{ mol})$ of 4,5-diazafluoren-9-one, 1.5 ml $(2.5 \times 10^{-3} \text{ mol})$ of glacial acetic acid, 50 ml of methanol and 7.8 ml $(2.2 \times 10^{-1} \text{ mol})$ of hydrazine hydrate (98%) was refluxed for 30 min. The hydrazone was recrystallized from ethanol, yield 3.5 g (65%); m.p. 198–208°C (ref.^[7] 208–211°C).

1.3 Preparation of 9-Diazo-4,5-diazafluorene (**3a**)^[7]: A suspension of 4.00 g (0.02 mol) of 4,5-diazafluorene hydrazone in 40 ml of benzene and 10 g of yellow mercuric oxide were placed in a 100-ml round-bottom flask capped with a calcium chloride tube. The reaction mixture was stirred in the dark for 1 d at room temp. and then filtered. The filtrate was concentrated under reduced pressure. Orange crystals of **3a** separated, yield 2.20 g (57%); m.p. 158–160°C. – IR (KBr): $\tilde{v} = 3040 \text{ cm}^{-1}$, (CH aromatic), 2090 (C=N₂), 1630, 1580 (C=N, C=C). – ¹H NMR (CDCl₃): $\delta = 7.38$ (m, 2H, aromatic), 7.89 (d, J = 7.84, 2H, aromatic), 8.70 (d, J = 4.24, 2H, aromatic). – C₁₁H₆N₄ (194.06): calcd. C 68.08, H 3.09, N 29.83; found C 67.65, H 3.11, N 28.43.

2. Reaction of 4,5-Diazafluorenylidene with Different Quenchers. – General Procedure: A weighed amount of 9-diazo-4,5-diazafluorene (**3a**) was dissolved in a certain volume of the quencher and placed in the photolysis cell. The mixture was irradiated, using a Hanovia high-pressure mercury lamp (450 W), under continuous magnetic stirring. The reaction was monitored by TLC. At the end of photolysis, the contents of the cell were quantitatively transferred into a distillation flask. The excess quencher was distilled under vacuum and the residue was separated by preparative TLC or column chromatography on silica gel or alumina. The products were identified using IR, ¹H NMR, ¹³C NMR, MS and elemental analysis. Results are indicated under each individual reaction and are also compiled in Tables 1 and 4.

2.1 Photolysis of 9-Diazo-4,5-diazafluorene (3a) in Styrene (5): A solution of 0.20 g (1.03 \times 10⁻³ mol) of **3a** in 20 ml of styrene was irradiated for 3 h. The excess of styrene was removed under vacuum. The residue was separated by preparative silica-gel thin-layer plate chromatography using ethyl acetate/methanol (20:1) as eluent. The major product was 4,5-diazafluorene-9-spiro-1'-(2'-phenyl)cyclopropane (16), which was recrystallized from ether/dichloromethane (20:1), yield 0.09 g (33%), m.p. $138-140^{\circ}$ C. – IR (KBr): \tilde{v} $= 3070 \text{ cm}^{-1}$ (CH of cyclopropane ring), 3020 (CH aromatic), 2900 (CH_2) , 1610, 1570 (C=N, C=C). – MS; m/z (%): 270.11 (100) $[M^+]$, 269.11 (72) $[M-H^+]$. – ¹H NMR (CDCl₃): $\delta = 2.30$ (dd, ${}^{3}J_{ac} = 6.35$ Hz, ${}^{2}J_{ab} = 8.61$ Hz, H_a, 1H), 2.32 (dd, H_b, ${}^{3}J_{bc} = 6.35$ Hz, ${}^{2}J_{ba} = 8.61$ Hz, 1H), 3.46 [(dd)t, H_c, ${}^{3}J_{ca} = {}^{3}J_{cb} = 6.35$ Hz, 1H], 6.45-8.78 (m, 11H, aromatic). $- {}^{13}C$ NMR (CDCl₃): $\delta =$ 32.04 (C-1'), 34.24 (C-2', CH), 21.15 (C-3', CH₂), 121.45-157.78 (16 C, aromatic). C₁₉H₁₄N₂ (270.11): calcd. C 84.44, H 5.18, N 10.37; found C 83.97, H 5.20, N 10.30. - The second fraction was

Table 4. ¹ H-NMR and ¹³ C-NMR	data of the	spirocyclopropanes	16-23
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Compd.	· · · · · · · · · · · · · · · · · · ·		¹ H NMR			¹³ C NMR				
	HA	H _B	H_{C}	CH_3	H-aromatic	C-1'	C-2'	C-3'	CH ₃	C-aromatic
16	2.30 (dd)	2.32 (dd)	3.46 (t)		6.45 - 8.78 (d, m, 11 H)	32.01	34.24	21.15		121.45 - 157.78 (16 C)
17	2.25 (m)	2.27 (dd)	3.39 (t)	2.31 (s)	6.50 - 8.70 (d, m, 10 H)	31.91	33.96	21.13	21.13	121.50 - 157.60 (16 C)
18	2.25 (d)	2.25 (m)	3.39 (dd)	3.79 (s)	6.50 - 8.73 (d, m, 10 H)	32.12	33,77	21.49	55.29	113.96 - 158.99 (16 C)
19	2.26 (m)	2.31 (dd)	3.39 (dd)		6.50 - 8.75 (d, m, 10 H)	32.06	33.50	21.14		113.85 - 157.92 (16 C)
20	2.30 (m)	2.43 (dd)	3.47 (dd)		6.40 - 8.78 (d, m, 10 H)	32.42	33.53	20.82		121.85 - 149.25 (16 C)
21	2.15 (d)	2.47 (d)		1.78 (s)	6.10 - 8.70 (d, m, 10 H)	36.06	39.09	28.43	24.67	121.30 - 158.76 (16 C)
22	2.55 (dq)		3.31 (d)	1.61 (d)	6.50 - 8.80 (d, m, 11 H)	36.99	41,60	30.22	14.14	120.55 - 159.52
23	2.50 (m)		3.54 (d)	1.39 (d)	6.50 - 8.80 (d, m, 22 H)	34.89	36.93	28.91	11.08	120.91 - 159.23

the ketazine **24**, yield 0.075 g (20%), m.p. >300°C (ref.^[6] >300°C). – IR (KBr): $\tilde{v} = 3050 \text{ cm}^{-1}$ (C–H aromatic), 1630, 1590 (C=N, C=C), 1400–800 (aromatic). – MS; *m/z* (%): 360 (100) [M⁺], 359 (72.62) [M–H⁺], 180 (37) [1/2 M⁺], 168 (61) [4,5-diazafluorene]. – ¹H NMR (CDCl₃): $\delta = 7.4-8.9$ (m, 12H, aromatic). C₂₂H₁₂N₆ (360.11): calcd. C 73.33, H 3.33, N 23.33; found: C 74.10, H 3.40, N 22.80.

2.2 Photolysis of **3a** in *p*-Methylstyrene (**6**): A suspension of 0.30 g $(1.5 \times 10^{-3} \text{ mol})$ of **3a** in 20 ml of *p*-methylstyrene was irradiated for 5 h and treated as before. The product 4,5-diazafluorene-9-spiro-1'2'(*p*-methylphenyl)cyclopropane (**17**) was eluted with ethyl acetate/methanol (25:2), yield 0.16 g (38%), m.p. 160–162°C. – IR (KBr): 3080 cm⁻¹ (CH of cyclopropane ring), 3020 (CH aroamtic), 2940 (CH₂, CH₃), 1600–1570 (C=N, C=C). – MS; *m/z* (%): 284.13 (16.62) [M⁺], 269.11 (4.7) [M–CH₃+]. – ¹H NMR (CDCl₃): $\delta = 2.25$ (dd, ³J_{ac} = 6.36 Hz, ²J_{ab} = 8.50 Hz, 1H, H_a), 2.27 (dd, ³J_{bc} = 6.36 Hz, ²J_{ba} = 8.50 Hz, 1H, H_b), 2.36 (s, 3H, CH₃), 3.39 [(dd)t, ³J_{ca} = ³J_{cb} = 6.36 Hz, 1H, H_c], 6.50–8.70 (m, 10H, aromatic). – ¹³C NMR (CDCl₃) $\delta = 31.91$ (C-1'), 33.96 (C-2', CH), 21.13 (C-3', CH₂), 21.02 (C of CH₃), 121.5–157.6 (16 C, aromatic). – The ketazine **24** was eluted (15 mg, 3%) similarly.

2.3 Photolysis of **3a** in p-Methoxystyrene (7): As in the case of pmethylstyrene, 0.30 g (1.5×10^{-3} mol) of **3a** was dissolved in 20 ml of p-methoxystyrene and irradiated for 4 h. The reaction mixture was separated by column chromatography on silica gel using ethyl acetate/methanol (10:1) as eluent. The first product was 4,5diazafluorene-9-spiro-1'-(2'-p-methoxyphenyl)cyclopropane (**18**), yield 0.18 g (40%), m.p. 163°C. – IR (KBr): $\tilde{v} = 3070$ cm⁻¹ (CH of cyclopropane ring), 3020 (CH aromatic), 2980 (CH₂, CH₃), 1610, 1595 (C=N, C=C), 1520 (CH₃, CH₂). – ¹H NMR (CDCl₃): $\delta = 2.25$ (m, 2H, H_A and H_B), 3.39 (t, J = 8.4 Hz, 1H, H_C), 3.79 (s, 3H, OCH₃), 6.50–8.73 (m, 10H, aromatic). – ¹³C NMR (CDCl₃): $\delta = 32.12$ (C-1'), 33.77 (C-2', CH), 21.49 (C-3', CH₂), 55.29 (C, OCH₃), 113.96–158.99 (16 C, aromatic). – Ketazine **24** was also isolated in trace amounts.

2.4 Photolysis of **3a** in p-Chlorostyrene (**8**): A solution of 0.30 g $(1.5 \times 10^{-3} \text{ mol})$ of **3a** in 20 ml of p-chlorostyrene was photolyzed for 6 h and treated according to the general procedure. The first product, 4,5-diazafluorene-9-spiro-1'-(2'-p-chlorophenyl)cyclopropane (**19**), yield 0.16 g (35%) was eluted with ethyl acetate/methanol (10:1). m.p. 190°C. – IR (KBr): $\tilde{v} = 3080 \text{ cm}^{-1}$ (CH of cyclopropane ring), 3020 (CH aromatic), 2980 (CH₂ aliphatic) 1600–1570 (C=N, C=C), 1500 (CH₂ aliphatic). – ¹H NMR (CDCl₃): $\delta = 2.26 \text{ (dd, } ^{3}J_{ac} = 6.46 \text{ Hz}, ^{2}J_{ab} = 8.42 \text{ Hz}, 1\text{ H}, \text{ H}_{a}$), 2.31 (dd, $^{3}J_{bc} = 6.46 \text{ Hz}, ^{2}J_{ba} = 8.42 \text{ Hz}, 1\text{ H}, \text{ H}_{a}$), 2.31 (dd, $^{3}J_{bc} = 6.46 \text{ Hz}, ^{2}J_{ba} = 8.42 \text{ Hz}, 1\text{ H}, \text{ H}_{a}$), 2.31 (dd, $^{3}J_{bc} = 6.46 \text{ Hz}, ^{2}J_{ba} = 8.42 \text{ Hz}, 1\text{ H}, \text{ H}_{a}$), 2.31 (dd, $^{3}J_{bc} = 6.46 \text{ Hz}, ^{2}J_{ba} = 8.42 \text{ Hz}, 1\text{ H}, \text{ H}_{a}$), 2.31 (dd, $^{3}J_{bc} = 6.46 \text{ Hz}, ^{2}J_{ba} = 8.42 \text{ Hz}, 1\text{ H}, \text{ H}_{a}$), 2.31 (dd, $^{3}J_{bc} = 32.06 (C-1'), 33.50 (C-2', CH), 21.14 (C-3', CH₂), 113.85–157.92 (16 C, aromatic). – C₁₉H₁₃N₂Cl (304.5): calcd. C 74.88, H 4.27, N 9.20; found C 74.59, H 4.25, N 9.14. – The second product was the ketazine$ **24**, yield 0.030 g (6%).

2.5 Photolysis of **3a** in p-Nitrostyrene (**9**): A solution of 0.30 g $(1.5 \times 10^{-3} \text{ mol})$ of **3a** in 20 ml of p-nitrostyrene was photolyzed for 6 h. The photolysate gave 4,5-diazafluorene-9-spiro-1'-(2'-p-nitrophenyl)cyclopropane (**20**), yield 0.14 g (30%), recrystallized from ether/dichloromethane (20:1), m.p. 242°C. – IR (KBr): $\tilde{v} = 3080 \text{ cm}^{-1}$ (CH of cyclopropane ring). – ¹H NMR (CDCl₃): $\delta = 2.36 \text{ (dd, H}_{a}, {}^{3}J_{ac} = 6.67 \text{ Hz}, {}^{2}J_{ab} = 8.44 \text{ Hz}, 1H, 2.43 \text{ (dd, H}_{b}, {}^{3}J_{bc} = 6.67 \text{ Hz}, {}^{2}J_{ab} = 8.44 \text{ Hz}, 1H, 2.43 \text{ (dd, H}_{b}, {}^{3}J_{bc} = 6.67 \text{ Hz}, {}^{2}J_{ab} = 8.44 \text{ Hz}, 1\text{ H}, {}^{-13}\text{C} \text{ NMR}$ (CDCl₃): $\delta = 32.42 \text{ (C-1')}, 33.53 \text{ (C-2', CH)}, 20.82 \text{ (C3', CH}_{2}), 121.85-149.25 \text{ (16 C, aromatic)}. – The ketazine$ **24**was separated in trace amounts.

2.6 Photolysis of **3a** in α -Methylstyrene (**10**): A mixture of 0.30 g (1.5×10^{-3} mol) of **3a** in 20 ml of α -methylstyrene was irradiated for 6 h. The residue was analyzed by column chromatography on silica gel using ethyl acetate/methanol (25:2) as eluent.

The first product was 4,5-diazafluorene-9-spiro-1'-(2'-methyl-2'-phenyl)cyclopropane (**21**), yield 0.23 g (54%), m.p. 178–180°C. – IR (KBr): $\tilde{v} = 3060 \text{ cm}^{-1}$ (CH or cyclopropane ring), 3010 (CH aromatic), 2980 (CH₂, CH₃), 1600, 1570 (C=N, C=C). – ¹H NMR (CDCl₃): $\delta = 1.78$ (s, 3H, CH₃), 2.15 (d, ³J_{ab} = 5.52 Hz, 1H, H_A), 2.47 (d, ³J_{ab} = 5.56 Hz, 1H, H_B), 6.1–8.7 (m, 11H, aromatic). – ¹³C NMR: $\delta = 36.6$ (C-1'), 39.09 (C-2'), 28.43, CH₂), 24.67 (C, CH₃), 121.3–158.76 (16 C, aromatic). – MS; *m*/z (%): 284 (70) [M⁺], 283 [M – H⁺], 269 (100) [M – CH₃⁺], 168 (13.72 [4,5-diazofluorene]. – C₂₀H₁₆N₂ (284): calcd. C 84.51, H 5.63, N 9.86; found C 83.86, H 5.67, N 9.82. – The second product was ketazine **24**, yield 0.015 g (3%).

2.7 Photolysis of **3a** in (E)- β -Methylstyrene (**11a**): A solution of 0.35 g (1.8 × 10⁻³ mol) of **3a** in 20 ml of (E)- β -methylstyrene was irradiated for 7 h and treated as before. Separation with column chromatography gave 4,5-diazafluorene-9-spiro-1'-(*trans-2'*-methyl-3'-phenyl)cyclopropane [(E)-**22**], yield 0.12 g (25%), m.p. 160–162°C. – IR (KBr): $\tilde{v} = 3070 \text{ cm}^{-1}$ (CH of cyclopropane ring), 3010 (CH aromatic), 2980 (CH₃), 1600, 1520 (C=N, C=C), 1445 (CH₃), 1400–700 (aromatic). – ¹H NMR (CDCl₃): $\delta = 1.61$ (d, ³J_{Me,a} = 6.30 Hz, 3H, H_{Me}), 2.55 (dd, ³J_{ac} = 7.93 Hz, ³J_{a,Me} = 6.30 Hz, 1H, H_a), 3.31 (d, ³J_{ac} = 7.93 z, 1H, H_c), 6.5–8.8 (d, m, 11H, aromatic). – C₂₀H₁₆N₂ (284): calcd. C 84.51, H 5.63, N 9.86; found C 83.73, H 5.97, N 9.10. – The second fraction was the ketazine **24**, yield 30 mg (5%).

2.8 Photolysis of **3a** in (Z)- β -Methylstyrene (**11b**): A mixture of **3a** (0.35 g, 1.8×10^{-3} mol) in (Z)- β -methylstyrene (**11b**) (20 ml) was irradiated for 13 h and then the excess of (Z)- β -methylstyrene was recovered by destillation under vacuum. The ¹H-NMR spectrum of the recovered styrene showed that no isomerization had taken place during the photolysis. The residue was treated as before. Separation gave a mixture (0.35 g, 68%) of (*E*)- and (*Z*)-cyclopropane **22** and **23** with a ratio of 1:3 according to the integration of ¹H-NMR spectrum, m.p. 140–145°C. – IR (KBr): $\tilde{v} = 3080$

cm⁻¹ (CH of cyclopropane), 3040 (CH; aromatic), 2980 (CH₃), 1600–1510 (C=N, C=C), 1410, 1190, 780 and 710. – ¹H NMR (CDCl₃): $\delta = 1.39$ (d, ³ $J_{Me,a} = 6.6$ Hz, 3H, *cis*-CH₃), 1.61 (d, ³ $J_{Me,a} = 6.30$ Hz, 3H, *trans*-CH₃), 2.50 (m, 2H, *cis*- and *trans*-H_a), 3.31 (d, ³ $J_{a,c} = 7.99$ Hz, 1H, *trans*-H_c); 3.54 (d, ³ $J_{a,c} = 9.5$ Hz; 1H, *cis*-H_c), 6.50–8.80 (m, 22H, *cis*- and *trans*-aromatic H). – ¹³C NMR (CDCl₃): $\delta = 11.08$, 14.06 (CH₃); 28.91, 30.15 (C-3'); 34.89, 36.93 (C-1'); 36.24, 41.53 (C-2'); 120.91–159.24 (arom. C). – C₂₀H₁₆N₂ (284): calcd. C 84.51, H, 5.63, N 9.86; found C 84.20, H 5.88, N 9.76. – MS: *m*/*z* (%): 285.13 (12) [M + 1⁺], 284.13 (61) [M⁺], 283.13 (12), [M – 1⁺], 269.11 (100) [M – CH₃⁺], 168.06 (10) [4,5-diazafluorene]. – The second fraction was the ketazine **24**, yield 0.10 g (15.4%), m.p. >300°C.

2.9 Photolysis of **3a** in 2,3-Dimethyl-2-butene (**12**): A suspension of 0.20 g $(1.03 \times 10^{-3} \text{ mol})$ of **3a** in 20 ml of 2,3-dimethyl-2-butene was irradiated for 16 h and the progress of the reaction was monitored with TLC until **3a** was completely consumed. The photolysate was separated using preparative silica-gel thin-layer plate (20 \times 20 cm) chromatography with ethyl acetate/methanol (20:1) as eluent. The only separated product was the ketazine **24**, yield 0.089 g (24%).

2.10 Photolysis of 3a in 2,3-Dimethyl-1,3-butadiene (13): A solution of **3a** (0.30 g, 1.5×10^{-3} mol) in 20 ml of 2,3-dimethyl-1,3butadiene was photolyzed for 4.5 h. The residue gave 4,5-diazafluorene-9-spiro-1'-(2'-methyl-2'-propen)cyclopropane (25), which was eluted with ethyl acetate/methanol (20:1) using column chromatography, yield 0.09 g (25%), m.p. 146°C. – IR (KBr): $\tilde{v} = 3090 \text{ cm}^{-1}$ (CH of cyclopropane ring), 3010 (CH aromatic), 2920 (CH₃, CH₂), 1620-1570 (C=N, C=C), 1480 (CH₃, CH₂). - MS; m/z (%): 248.08 (22.19) $[M^+]$, 233.06 (26.84) $[M - CH_3^+]$, 205.05 (13.27) $[M - C_3H_5^+]$, 168.06 [4,5-diazafluorene]. – ¹H NMR (CDCl₃): δ = 1.25 (s, 3H, CH₃), 1.58 (s, 3H, CH₃), 1.96 (d, 1H, H_A, J_{BA} = 5.38 Hz), 2.30 (d, 1H, H_B, J_{AB} = 5.38 Hz), 5.09 (s, 2H, H_C and H_D), 7.13–8.71 (dd, d, 6H, aromatic). – ¹³C NMR (CDCl₃): δ = 20.57 (C-6', CH₃), 27.79 (C-7', CH₃), 21.29 (C-2', CH₂), 40.34 (C-1'), 35.53 (C-3'); the signals of C-4', C-5' and of the aromatic carbon atoms appeared in the aromatic range. $-C_{17}H_{16}N_2$ (248.13): calcd. C 82.21, H 6.45, N 11.29; found C 82.03, H 6.41, N 11.28. - Ketazine 24 was also eluted, yield 0.050 g (9%).

2.11 Photolysis of **3a** in Absolute Methanol (**14**): A solution of 0.30 g (1.5×10^{-3} mol) of **3a** in 20 ml of absolute methanol was irradiated for 3 h and monitored by TLC. The excess of methanol was evaporated and the products were separated on a silica-gel chromatography column using ethyl acetate/methanol (25:1) as eluent. The first product was 9-methoxy-4,5-diazafluorene (**26**), yield 0.075 g (25%), which recrystallized from dichloromethane, m.p. 117°C. – IR (KBr): $\tilde{v} = 3050 \text{ cm}^{-1}$ (CH aromatic), 2860 (CH₃), 1600, 1570 (C=N, C=C), 1080 (OCH₃). – MS; m/z (%): 198.09 (24.4) [M⁺], 197.08 (6) [M – H⁺], 183.07 (100) [M – CH₃⁺], 167.07 (36) [M – OCH₃⁺]. – ¹H NMR (CDCl₃): $\delta = 3.1$ (s, 3H, CH₃), 5.65 (s, 1H, CH), 7.31–8.75 (dd, 6H, aromatic). – C₁₂H₁₀N₂O (198.09): calcd. C 72.73, H 5.05, N 14.14; found C 71.62, H 5.04, N 14.55. – The second product was the ketazine **24**, yield 0.095 g (18%).

2.12 Short-Period Photolysis of **3a** in Methanol (14): A solution of **3a** (0.30 g, 1.5×10^{-3} mol) in 20 ml of absolute methanol was irradiated for 35 min. Analysis of the photolysate, after evaporation of the excess methanol, with HPLC technique using authenic samples showed the presence of the starting diazo compound **3a**, the ether **26**, in addition to the ketazine **24**. No peak corresponding to the diazirine was detected. The residue was separated as usual by column chromatography. The first fraction (0.015 g, 5%) was identified as 9-methoxy-4,5-diazafluorene (26) which eluted with ethyl acetate/methanol (25:1), the second fraction was the starting diazo compound 3a (0.20 g, 69%), and the third fraction was the ketazine 24 in trace amounts.

2.13 Photolysis of **3a** in Benzene (**15**): In 20 ml of absolute benzene, 0.30 g (1.5×10^{-3} mol) of **3a** was dissolved and the solution was irradiated for 4 h and processed as before. The first product separated was mixture of two isomers, norcaradiene **27** and cycloheptatriene derivative **27**', identified and followed at different low-temperatures by ¹H NMR yield (0.16 g, 44%), m.p. 179–180°C. – C₁₇H₁₀N₂ (242.09): calcd. C 84.29, H 4.13, N 11.37; found C 83.83, H 4.80, N 11.22. – The second fraction was the ketazine **24** yield 23 mg (7%).

3. Competition Experiments

3.1 Photolysis of 3a in Styrene Mixtures. – General Procedure: Competition experiments were carried out by dissolving 0.50 g $(2.58 \times 10^{-3} \text{ mol})$ of 9-diazo-4,5-diazafluorene (3a) in an equimolar mixture of styrene (5) (0.52 g, 5×10^{-3} mol) and each of the *p*-substituted styrenes 2-6 (5×10^{-3} mol) in 20 ml of ether. After photolysis and workup as described in the general procedure, the cyclopropane mixtures were analyzed by quantitative HPLC using standard solutions of 16–20. Results are shown in Table 3.

3.2 Photolysis of **3a** in Mixtures of Methanoll2,3-Dimethyl-1,3butadiene: 0.05 g (2.5×10^{-3} mol) of **3a** was dissolved in 20 ml of a mixture of methanol and 2,3-dimethyl-1,3-butadiene (variable amounts) and irradiated for 4.5 h. The reaction mixtures were concentrated and the residues were analyzed by ¹H NMR (CDCl₃, the ether/cyclopropane ratios were determined in each case. Results are shown in Table 2.

3.3 Reactions of **3a** with Dimethyl Acetylenedicarboxylate^[23]: A suspension of 0.20 g (1.03 \times 10⁻³ mol) of **3a** in 2 ml of ether was placed in a round-bottom flask and magnetically stirred. Drops of dry dichloromethane were added until 3a had completely dissolved. Then 0.15 g (1.05 \times 10⁻³ mol) of dimethyl acetylendicarboxylate was added with stirring. The flask was fitted with a calcium chloride drying tube, stirred in the dark at room temperature for 2 h, allowed to stand for 1 d in the dark and monitored with TLC. A grey substance, 28, was separated, yield 0.10 g (29%), filtered off and identified using IR, NMR and MS techniques, m.p. 145°C. -IR (KBr): $\tilde{v} = 3050 \text{ cm}^{-1}$, 3030 (CH aromatic), 2980 (CH₃), 1750 (C=O), 1650, 1590 (C=N, C=C), 1350-1340 (OCH₃), 1280 (CO). - MS; m/z (%): 336.09 (6) [M⁺], 308.08 (9) [M - N₂⁺], 305.06 (13.6) [M - 2 CH₃⁺], 219.06 (23.5) [M - 2 CO₂CH₃⁺]. C17H12N4O4 (336.09): calcd. C 60.71, H 3.57, N 16.67; found C 59.63, H 3.25, N 15.93.

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[[] \approx] Dedicated to Professor *H. D. Scharf* on the occasion of his 65th birthday.

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