Chemistry of 1-Alkylfluorenylidenes. Steric Effects on Arylcarbene Reactivities[†]

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Abstract: 9-Diazofluorenes (RDAF, **1**) having a series of alkyl (R) groups from Me to tBu at the 1-position were prepared and decomposed to generate the corresponding fluorenylidenes (RFL, **2**) under various conditions in order to examine steric effects on the reactivities of carbenes. Thus, in cyclohexane, singlet fluorenylidenes (^{1}RFLs) gave 9-cyclohexylfluorenes while triplet states (^{3}RFLs) underwent H abstraction to give 9-fluorenyl (RFLH$^\bullet$), which eventually led to fluorene (**4**, RFLH$_2$) and 9,9′-bifluorenyl (**5**), and the ratio of the triplet products to the singlet was increased as more bulky R groups were introduced at the 1-position. These results are interpreted in terms of the steric effects on singlet reactivity, which requires formation of two bonds simultaneously. Generation of tBuFL resulted in the almost exclusive formation of intramolecular reaction products which involved not only insertion of carbene into the δ-C−H bonds of the *tert*-butyl group but also insertion of the 1,5-biradical, followed by neophyl-type rearrangement. The results are understood as indicating that abstraction of the δ-H by ^{3}tBuFL gains over the concerted intramolecular C−H insertion in ^{1}tBuFL. Generation of 1-RFL (R = Et, iPr, tBu) in the gas phase at high temperature gave intramolecular reaction products both in singlet and in triplet states, but the ratio of the singlet to the triplet product increased in going from Et to iPr to tBu presumably due to the increased opportunities of ^{1}FL to be trapped by δ-C−H bonds. Spectroscopic studies using matrix isolation techniques as well as laser flash photolysis were also carried out to gain information on the intermediates.

The chemical and physical properties of aromatic carbenes have recently been the object of continued and ever-increasing interests.[1] A part of the interest obviously comes from the hope of probing the structural features that control the chemical properties of these highly reactive intermediates. The reactions of carbenes are shown to be sensitive to electronic perturbation, probably due to the fact that a small shift in energy may change the spin multiplicity of the ground state. For example, the triplet state of fluorenylidene (FL) has been estimated to be less than 1.9 kcal/mol.[2] The singlet−triplet energy difference, ΔG_{ST}, is increased by introducing electron-withdrawing groups, and the chemical properties are changed.[2] Thus, the chemical properties exhibited by FL are characteristic of both a singlet and a triplet as a consequence of the near degeneracy of these two states. On the other hand, for 2,7-dihalofluorenylidene, the gap between singlet and triplet is too large to be overcome within the lifetime of the triplet carbene and hence it behaves as a classical triplet carbene.[2] Addition of electron-donating groups stabilizes the singlet state and inverts this order. In this approach, the substituent effect is transmitted through the π-system of the arene to the p-type orbital of the carbene, and the properties of the carbene are therefore controlled by raising or lowering the energy of this orbital.[2]

The geometry of a carbene is also an important factor controling its reactivity by changing ΔG_{ST}. Thus, theory predicts that forcing CH$_2$: to adopt a smaller bond angle raises the energy of the triplet faster than that of the singlet.[3] This phenomenon is employed to explain the difference in ΔG_{ST} between FL and diphenylcarbene (DPC). The carbene−carbon bond angle in triplet FL ($\Delta G_{ST} \sim 2$ kcal/mol) is 110°,[4] while the corresponding angle in triplet DPC ($\Delta G_{ST} \sim 4$ kcal/mol) is 140°.[5]

A third factor which should play a role in controlling the reactivities of carbenes is the kinetic effect caused by steric requirement for the reaction. For instance, the insertion selectivity of a singlet carbene into C−H bonds is often affected by steric requirements in the transition state.[6] The stereoselectivity in the addition of singlet carbenes to olefins is also controlled by the concerted nature of the reaction.[7]

The steric factor has been studied less systematically and is therefore less satisfactorily understood. During our attempts to stabilize triplet arylcarbenes kinetically in the hope of generating persistent carbenes,[8] the need for a deeper insight into this effect become apparent. We therefore embarked on a study of the steric effect on the reactivity of arylcarbenes. FL is especially suitable for this study because (i) the electronic effect is relatively well-understood,[2] (ii) the bond angle at the carbene center does not change significantly, and (iii) the

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[†] Dedicated to Prof. Dr. Manfred Regitz on the occasion of his 60th birthday.

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(2) See for review: Schuster, G. B. *Adv. Phys. Org. Chem.* **1986**, *22*, 311. See also: Li, Y.-Z.; Schuster, G. B. *J. Org. Chem.* **1986**, *51*, 3804. Li, Y.-Z.; Schuster, G. B. *J. Org. Chem.* **1987**, *52*, 3975. Li, Y.-Z.; Schuster, G. B. *J. Org. Chem.* **1987**, *52*, 4460. Rak, S. F.; Lapin, S. C.; Falvey, D. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1987**, *109*, 5003.

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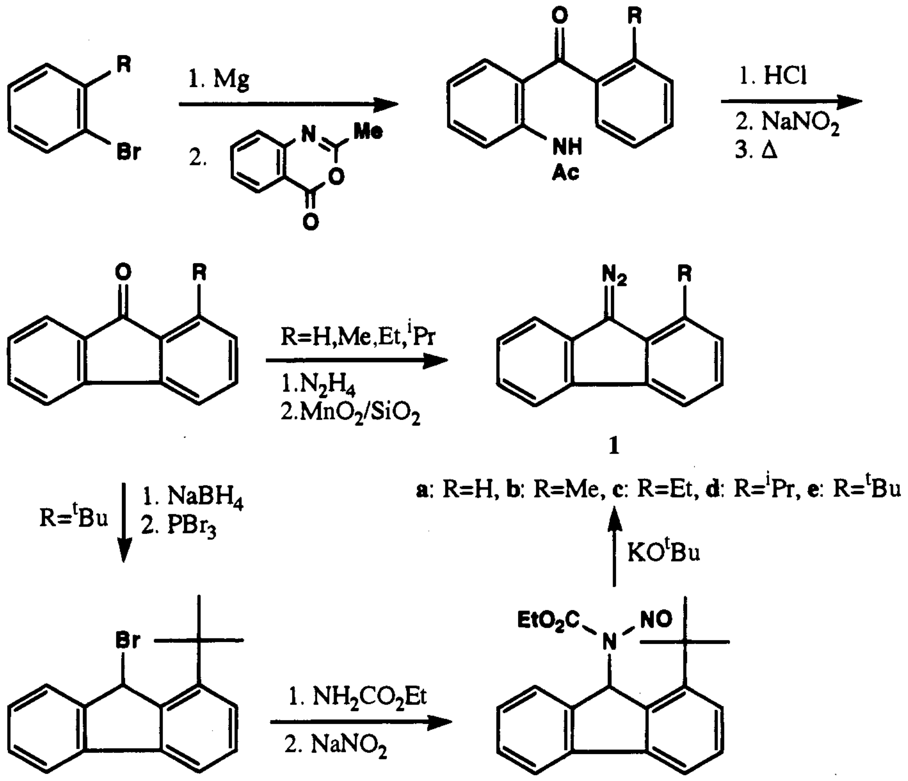
Scheme 1



carbene center is less susceptible to be trapped by proximate functional groups within the molecule due to the inherently rigid structure. Thus, we generated and investigated a series of 1-alkyl-9-fluorenylidenes from the corresponding diazofluorenes not only in fluid solution but also in the gas phase by product analysis combined with flash photolysis techniques and found that, as more bulky ortho substituents are introduced, the intermolecular reactions of singlet FL are significantly suppressed, while reactions due to the triplet become more predominant either intermolecularly or intramolecularly.

Results and Discussion

Preparation of 1-Alkyl-9-diazofluorene (RDAF, 1). 1-Alkyl-9-fluorenones were prepared from the corresponding 2-alkyl-2′-aminobenzophenones which were obtained by reaction of (2-alkylphenyl)magnesium bromides with acetylanthranil.[9] The diazo compounds **1a**–**d** were conveniently prepared by conventional procedures, viz. hydrazonation of the ketone with N_2H_4, followed by oxidation of the resulting fluorenone hydrazone. Oxidation could be performed with mercury(II) oxide, but oxidation using MnO_2 supported on SiO_2 proceeded much more rapidly to form the diazo compound in a purer form. Since 1-*tert*-butylfluorenone did not undergo hydrazonation, the diazo compound **1e** was prepared by base-catalyzed decomposition of the corresponding *N*-nitrosocarbamate which was prepared from 1-*tert*-butyl-9-bromofluorene (Scheme 1). All of the diazofluorenes were obtained as rather stable solids which could be kept in a refrigerator for several months without any appreciable decomposition.

Reactions of 1-Alkylfluorenylidene (1-RFL, 2) with Methanol. Reactions of fluorenylidene (FL, **2a**) in methanol have been well-studied.[2] Thus, generation of **2a** by photolysis of DAF (**1a**) in methanol results in the almost exclusive formation of 9-methoxyfluorene (**3a**), which is explained by trapping of the nascent singlet FL by the solvent OH bond; methanol is generally recognized as one of the most efficient trapping reagents for most singlet carbenes.[1] The ether is occasionally accompained by the formation of fluorene (**4**) as well as 9,9′-bifluorenyl (**5**) especially when the irradiation is carried out with shorter wavelength light ($\lambda > 300$ nm). The products like **4** and **5** are usually believed to be formed from triplet states of the carbenes by hydrogen abstraction from the solvent to yield first the 9-fluorenyl radicals (**6**), which then undergo either abstraction of a second hydrogen atom or dimerize. However, control experiments demonstrate that 9-methoxyfluorene (**3a**) is photoexcited under these conditions and undergoes C–O bond cleavage to generate the same radicals **6**, which consequently can produce **4** and **5**.[10]

In order to avoid ambiguity of the origin of the radical products, photolysis of RDAF (**1b**–**e**) in degassed methanol was carried out with light of $\lambda > 350$ nm from a high-pressure mercury arc lamp. This resulted in the formation of 9-methoxyfluorenes (**3b**–**e**) almost exclusively, along with only trace amounts (~1%) of fluorenes (**4b**–**e**) and 9,9′-bifluorenyls (**5b**–**e**), regardless of the substituents at the 1-position (Scheme 2, Table 1). These results suggest that the chemistry of 1-RFL (**2**) in methanol is essentially the same as that of FL: the singlet state is efficiently trapped by the OH bond of the alcohol to produce **3** before it undergoes intersystem crossing (isc) to the triplet. Thus, even the *tert*-butyl group at the 1-position does not affect the singlet state reaction with the alcohol.

Reactions of 1-RFL with Cyclohexane. Photolysis of DAF in cyclohexane produces 9-cyclohexylfluorene (**7**) as the main product along with fluorene (**4**) and bifluorenyl (**5**). That **7** is formed almost exclusively from the singlet FL by direct C–H insertion while **4** and **5** are produced from the triplet by way of 9-fluorenyl is shown by generating FL in a binary mixture of $C_6H_{12}-C_6D_{12}$ (vide infra).[2] Control experiments show that **7**

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(9) Lothrop, W. C.; Goodwin, P. A. *J. Am. Chem. Soc.* **1943**, *65*, 363.

(10) Tomioka, H.; Nakamura, H.; Izawa, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 1070.

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Scheme 2

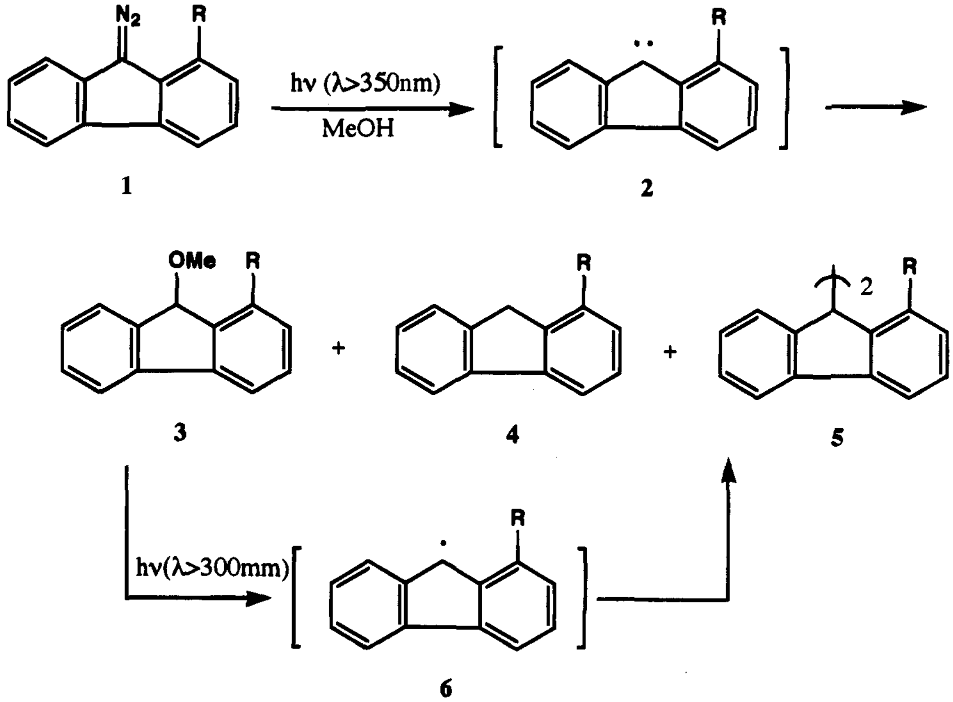

Table 1. Photolysis[a] of **1** in MeOH

	yield, %[b]		
1	**3**	**4**	**5**
1a	95	*c*	*c*
1b	95	*c*	*c*
1c	95	*c*	*c*
1d	97	*c*	*c*
1c	98	*c*	*c*

[a] Irradiations were carried out on 5 mL of degassed solutions of **1** with a 300 W high-pressure mercury arc equipped with a Corning CS-052 filter. [b] Determined by GC on the basis of **1** used. [c] Less than 1%.

is not photodecomposed even upon irradiation with shorter wavelength light.[11]

Reactions of RFL except **1e** in cyclohexane were similar to those observed with FL. Thus, photolysis of RDAF (**1b**−**d**) in degassed cyclohexane at room temperature afforded 1-alkyl-9-cyclohexylfluorenes (**7**) along with 1-alkylfluorenes (**4**) and 9,9′-bis(1-alkylfluorenyls) (**5**). The product distributions were, however, found to be somewhat sensitive to the bulkiness of the 1-substituents; the ratio of **7** to **4** plus **5** decreased significantly as more bulky alkyl groups were introduced at the 1-position (Scheme 3, Table 2).

The most probable explanation of the formation of **7** is direct insertion of singlet **2** into a carbon−hydrogen bond of the solvent. However, the formation of a significant amount of the bifluorenyl (**5**), especially when the fluorenylidenes carry an alkyl group at the 1-position, might indicate that the solvent adduct **7** may also be formed in a two-step abstraction−recombination sequence proceeding through a free radical. In order to distinguish between these two pathways, the irradiation of **1d** was carried out in a 1:1 mixture of C_6H_{12} and C_6D_{12}, and the deuterium distribution in the products were determined by mass spectrometric analysis. This clearly showed that the direct insertion products, i.e., **7d**-h_{12} and **7d**-d_{12}, were formed almost exclusively (>95%) while the scrambled products were present in only less than 5% yield. The results clearly indicate that the C−H insertion product is formed almost exclusively (>95%) from the singlet carbene regardless of the substituents at the 1-position. An isotope effect on the formation of **7** was estimated to be 1.83 ± 0.1 on the basis of the product distribution, which is again similar to that observed for singlet FL C−H insertion. It is generally observed that the isotope effect for abstraction of hydrogen by a triplet carbene is ca. 4−8 while insertion into a C−H bond by a singlet carbene proceeds with an isotope effect of only ca. 1−2.[2,12] In contrast, the bifluorenyl (**5d**) formed in this reaction is a mixture of the d_0 and d_1 compounds, again supporting the well-known fact from unsubstituted FL chemistry that bifluorenyl formation must involve combination of free 9-fluorenyl radicals.[2]

Thus, the above control experiments demonstrate that, although the product distributions are significantly changed as one introduces alkyl groups at the 1-position, the mechanism of the formation of each product is not changed. In other words, as more bulky groups are introduced, reaction from the triplet carbene increases at the expense of the singlet-derived product. This can be explained in terms of the steric hindrance of the direct insertion of the singlet carbene into the C−H bond of the solvent. At least two mechanisms have been proposed for the singlet carbene C−H insertion process: one is known as the Doering−Skell mechanism,[13] which asserts that a triangular transition structure is involved, while the other, known as the Benson−DeMore mechanism,[14] asserts that the carbene attacks the hydrogen atom via a linear transition structure. Ab initio calculations on the simplest singlet carbene reaction fully support the triangular transition state, while analogous calculations for the triplet insertion favor the linear transition state.[15] Presumably, as has been verified in many experimental works,[1,2,16] the

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[12] Bethell, D.; Newall, A. R.; Wittaker, D. J. *J. Chem. Soc. B* **1971**, 23.

[13] (a) Skell, P. S.; Woodworth, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 4496. (b) Doering, W. E.; Prinzbach, H. *Tetrahedron* **1959**, *6*, 24.

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[15] (a) Baskin, C. P.; Bender, C. F.; Bauschlicher, C. W.; Shaefer, H. F. *J. Am. Chem. Soc.* **1974**, *96*, 2709. (b) Bauschlicher, C. W.; Bender, C. F.; Schaefer, H. F. *J. Am. Chem. Soc.* **1976**, *98*, 3072. (c) Kollmar, H.; Staemmler, V. *Theor. Chim. Acta* **1979**, *51*, 207.

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Scheme 3

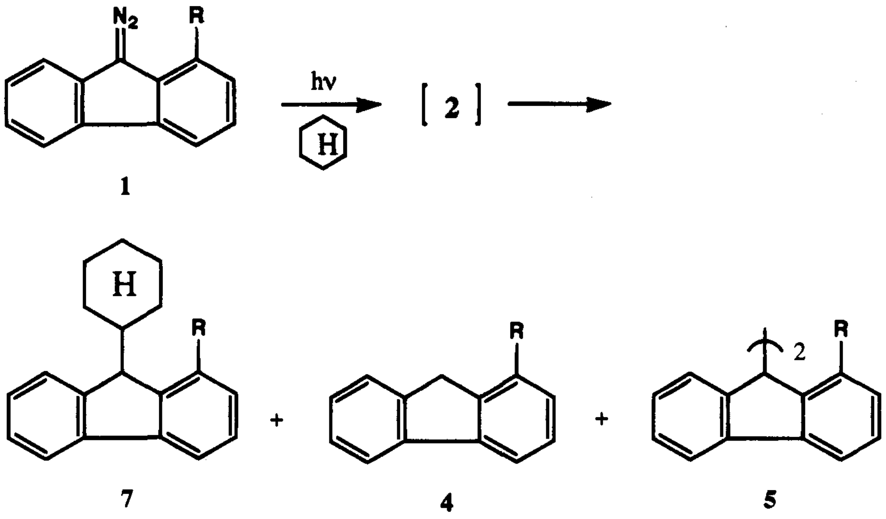


Table 2. Photolysis[a] of **1** in Cyclohexane

1	yield, %[b]			7/(4 + 5)
	7	**4**	**5**	
1a	65.4	7.8	9.4	3.80
1b	63.9	2.2	17.4	3.26
1c	71.3	1.1	25.9	2.64
1d	63.5	2.9	31.6	1.84
1e[d]	5.2	*c*	*c*	

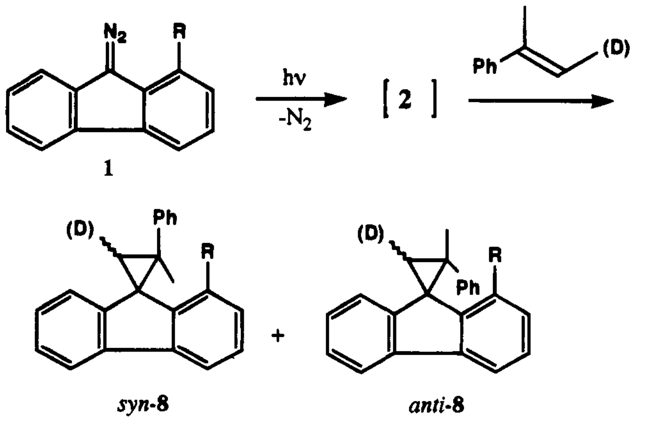
[a-c] See footnotes a–c to Table 1. [d] **9e** (58.0%) and **10e** (32.4%) were formed.

singlet FL must also approach the C–H bond in a perpendicular fashion in order to go through the triangular transition structure; this evidently is sensitive to steric factors. Thus, as more bulky groups are introduced in the 1-position, this perpendicular approach will be subject to steric repulsion by the 1-substituent and the singlet process therefore becomes less favorable. Consequently, the hydrogen abstraction reaction from the triplet carbene will be able to play a significant role since this process requires a linear transition state geometry.[15] It is therefore less sensitive to steric factors. Support is lent to this explanation by the observation that the ratio of **7** to **4** plus **5** was found to be 4.46 when an ethyl group is introduced at the 2-position of FL, in which case steric factors become unimportant.

The steric hindrance operating in the direct C–H insertion by singlet FL was assessed in competition experiments using cyclohexane and ethanol. Thus, the relative rate of the C–H insertion ($k_{\mathrm{C-H}}$) to O–H insertion ($k_{\mathrm{O-H}}$) determined from the ratios of products and substrates was 0.26 for unsubstituted FL. This ratio decreased to 0.055 as a 1-ethyl group was introduced, while for 2-ethyl FL, it was 0.14. At least three plausible mechanisms have been proposed for the O–H insertion of singlet carbenes: (i) one-step insertion into the OH bond, (ii) electrophilic attack of the carbene at oxygen followed by proton transfer, and (iii) protonation of the carbene.[1,12] It has been shown recently that diphenylcarbenes undergo protonation by alcohol,[17] whereas an ylidic intermediate is suggested to be involved in the reaction of FL with alcohol as would be expected from its cyclopentadienylidene structure.[2,18] Regardless of which mechanism is operating, however, the approach of FL to the O–H bond of ethanol is much less sensitive to steric factors than that to cyclohexane in the light of substituents around the reaction center involved in the transition states. Thus, FL tends to prefer attack on ethanol as the carbenic centers become more crowded.

Reaction of 1-RFL with α-Methylstyrene. Most carbenes undergo cycloaddition to the double bond of alkenes to produce cyclopropanes. The stereochemical outcome of these cyclopropanation reactions has often been used to diagnose the spin multiplicity of the reacting carbene: stereospecific cyclopropanation has long been associated with singlet carbenes, and nonstereospecific addition, with triplets.[1] The alkene we chose for this study was (*E*)-β-deuterio-α-methylstyrene which has been used often to diagnose the multiplicity of fluorenylidenes.[2] Irradiation of 1-iPrDAF (**1d**) in acetonitrile containing 2.0 M α-methylstyrene gave the expected cyclopropanes **8** in ca. 80% yield. The ^{1}H NMR spectrum of the product shows the presence of two well-resolved sets of signals of cyclopropyl and methyl hydrogens ascribable to *syn*- and *anti*-cyclopropanes, as expected from the configuration of Ph with respect to the 1-iPr group.

Scheme 4



Similar irradiation of **1d** in the presence of (*E*)-β-deuterio-α-methylstyrene afforded products whose ^{1}H NMR spectra consisted of four sets of hydrogens ascribable to all four possible cyclopropanes. Retention of configuration (defined as [retained – inverted]/[retained + inverted]) was calculated to be 14%. Under these conditions FL is known to react with 50% retention of configuration.[2] These observations are again explained in terms of the increased steric hindrance by the bulky 1-alkyl group toward the concerted addition of the singlet FL to the double bond.

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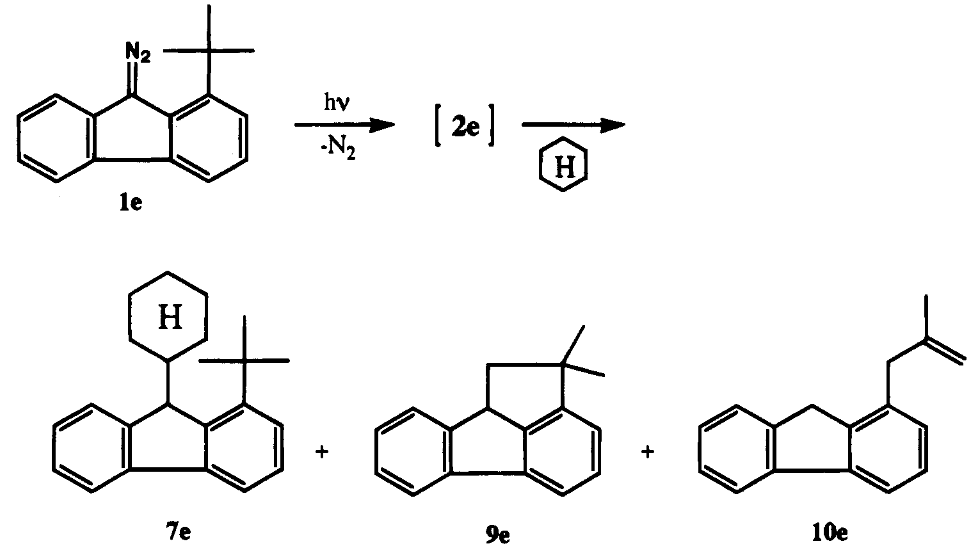
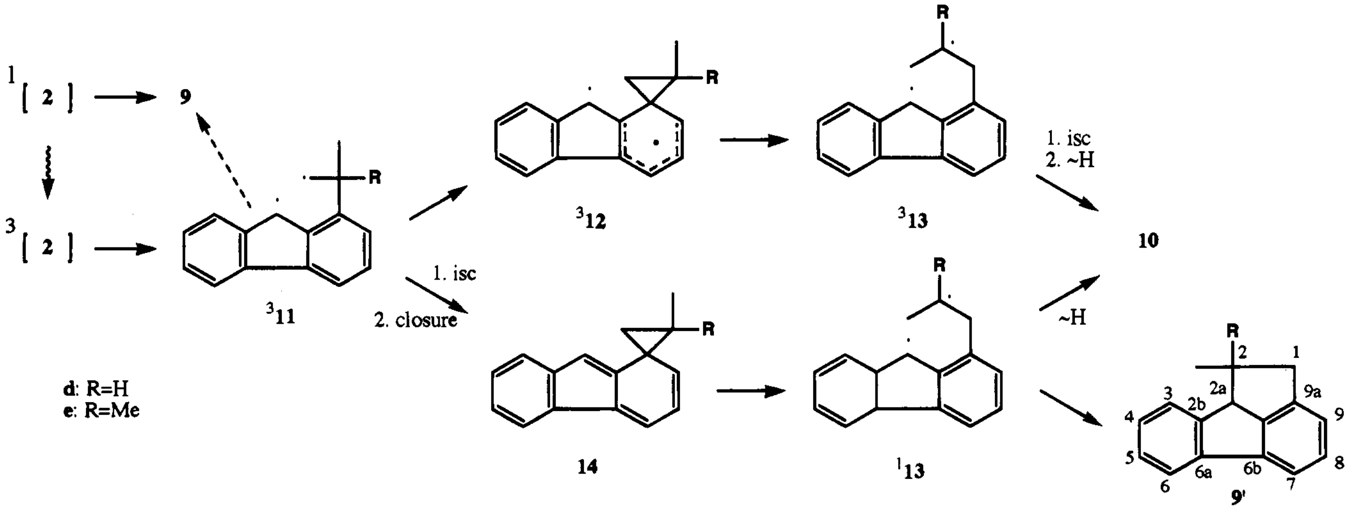
Scheme 5



Scheme 6



Reactions of 1-*tert*-Butylfluorenylidene (2e). As one could expect from the increased steric congestion around the carbenic center, the chemistry of **2e** in cyclohexane solution was completely different from that observed for the other 1-RFLs. Thus, the carbene decayed mainly by intramolecular interaction with the *tert*-butyl group at the 1-position, the solvent adduct formation being a minor process (Scheme 5, Table 2).

Two intramolecular reaction products, i.e., **9e** (58.0%) and **10e** (32.4%), were produced. The formation of **9** can be explained in terms of direct insertion of singlet carbene into the C—H bond of the *tert*-butyl group, whereas the formation of **10** must include rearrangement. Presumably, carbene **2e** is forced to undergo intramolecular reaction owing to the steric repulsion of an approaching external substrate. Direct intramolecular C—H insertion forming **9** is, however, also not an energetically very favorable reaction because the approach of the carbenic center to the *tert*-butyl C—H bonds (presumably in perpendicular fashion) is restricted due to the rigidity of the fluorenyl structure. The X-ray analysis of indenofluorene (**9c**, R = R′ = H), for instance, indicates that strain causes deformation of one of the aromatic rings to a flat unsymmetrical boat structure and that this aromatic ring reacts with dienophiles as well as O_2.[19] Thus, the rate of this reaction from the singlet state is retarded to such an extent that intersystem crossing to the triplet can compete. The triplet carbene thus formed is again forced to undergo intramolecular hydrogen abstraction to generate a 1,5-biradical intermediate **11**, which then undergoes rearrangement to a new, more stable 1,5-biradical **13**. 1,6-Hydrogen migration in **13** will produce **10**. The rearrangement of **11** to **13** is analogous to a neophyl rearrangement which is suggested to proceed through a spirocyclopropyl-type biradical intermediate or transition (**12**).[20] However, the rearrangement is known to require quite a large activation energy and therefore the rearrangement through **12** could be slow.[20] It may be that the rearrangement proceeds instead through the spirocyclopropyl intermediate **14**, which can be formed by intersystem crossing (isc) of the triplet biradical **11**, followed by ring closure (Scheme 6). The fluorene **9** could also be formed from the biradical intermediate **11** by isc followed by intramolecular coupling. However, this possibility was eliminated by the following control experiments. Thus, when the photolysis of **1e** was carried out in the presence of 1,4-cyclohexadiene, 2-*tert*-butylfluorene (**4e**) was produced at the almost complete expense of **10** whereas the formation of **9** was little affected, thus

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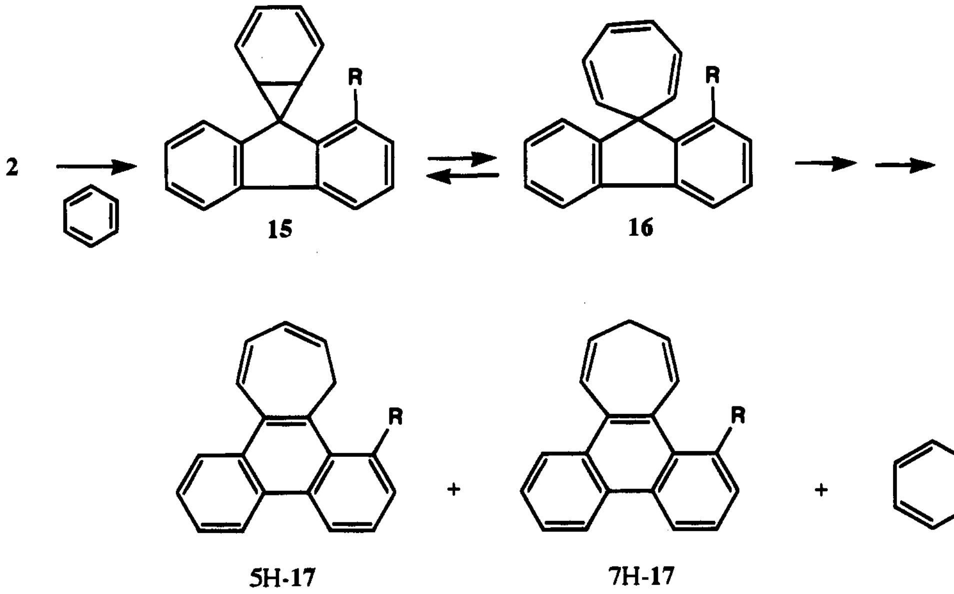
Scheme 7



indicating that **9** and **10** are not produced from a common intermediate. Accepting that **4e** is formed from the triplet carbene **2e** by a double hydrogen abstraction from the diene,[21] the results are best interpreted as indicating that, while the singlet carbene undergoes C–H insertion even in the presence of the diene quencher, the triplet state is trapped efficiently by the diene to produce **4e** as they are produced by isc from the singlet.[22]

Reactions of 2 with Benzene. Reactions of photolytically generated FL with benzene have been intensively studied by Dürr and his co-workers,[23] who have shown that spironorcardiene (**15**) in equilibrium with its valence isomer (**16**) can be isolated if the photolysis is carried out with a long-wavelength filter (λ > 360 nm) and if careful work-up procedures are applied. The carbenic dimer **18** is formed as well. The norcaradienes **15** and **16** easily undergo skeletal rearrangement during irradiation with shorter wavelength light (λ > 300 nm) and under work-up procedures to give benzocycloheptatriene derivatives 5*H*- and 7*H*-**17** (Scheme 7).

Generation of 1-methyl (**2b**) and 1-ethyl FLs (**2c**) by photolysis (λ > 300 nm) of the diazofluorenes in benzene solution also produced the benzocycloheptatrienes **17** as major adducts, along with radical dimers (**5**) and reduction products (**4**) obviously derived from 9-fluorenyl radicals. Formation of carbene dimers **18** albeit in small amount was also revealed by GC–MS. Appreciable formation of the radical products **4** and **5** obviously derived from the triplet carbene even in benzene, usually regarded as a poor hydrogen donating solvent, is rather surprising and indicates that the reaction of the singlet carbene to give **15** again has become energetically unfavorable owing to the steric repulsion by the 1-alkyl groups. Thus, the singlet decays to the triplet. In the reaction of FL (**2a**) in benzene, an appreciable amount of carbene dimer **18a** was isolated.[23] This implies that the reaction with benzene is not very efficient even for the parent singlet FL and thus carbene undergoes isc to form the triplet. The triplet FL then must decay by dimerization to produce bifluorenylidene (**18a**), presumably because the abstraction of hydrogen from solvent benzene is a highly inefficient process. Dominant formation of bifluorenyl **5** over **18** in the reaction of 1-alkylfluorenylidenes therefore suggests that the dimerization process becomes energetically much less favorable for 1-alkyl FL due to steric repulsion caused by the 1-alkyl group,[24] and the triplet carbene is therefore forced to abstract hydrogen even from the solvent benzene. In accord with this explanation, generation of **2c** in C_6D_6 resulted in the formation of the benzene adducts **17** almost exclusively, no radical dimers being detected.

Table 3. Photolysis[a] of **1** in Benzene

1	yield, %[b]			
	17[c]	**4**	**5**	**18**
1a[d]	45–50			3.5
1b	70.9	1.9	13.9	5.2
1c	59.1	8.9	19.4	3.4
1d[e]	56.2	trace	17.1	3.5
1e[f]	*g*	*g*	*g*	*g*

[a] Irradiations were carried out with a 300 W high-pressure mercury arc with a pyrex filter. [b] Determined by GC. [c] Approximately 3:1–4:1 mixtures of 5*H* and 7*H* isomers. [d] Data reported by Dürr et al.[23] [e] **9d** (8.8%) and **10d** (8.1%) were formed. [f] **9e** (56.8%) and **10e** (41.1%) were formed. [g] Less than 1%.

Support is lent to the above explanation by the reaction of 1-isopropyl FL (**2d**), which produced appreciable amounts of intramolecular reaction products **9d** and **10d** in competition with the formation of benzene adducts **17d** as well as the radical dimer **5d**. Formation of the intramolecular products, which are not detected at all in the reaction in cyclohexane, clearly suggests that both addition to and hydrogen abstraction from benzene become more unfavorable as a more bulky alkyl group is introduced at the 1-position. The carbene therefore tends to interact intramolecularly with C–H bonds in spite of the strain energy accompanying the formation of **9d** and **10d**. These

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(21) The excellent hydrogen donor property of 1,4-cyclohexadiene has been recognized in its reaction with triplet benzophenone: Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 6393.

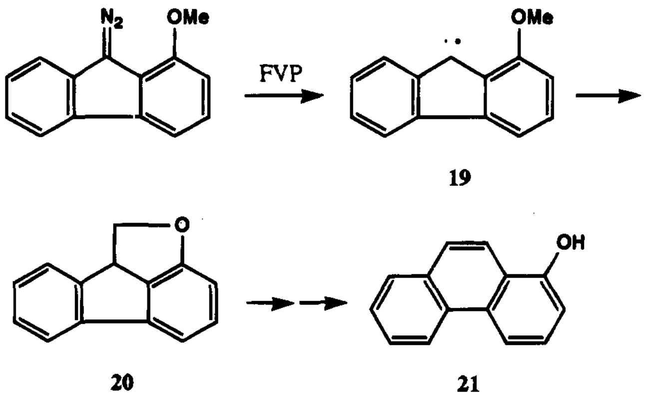
(22) It is well-documented that triplet arylcarbenes generated in good hydrogen donor solvents undergo H abstraction.[1] See also: Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 283.

(23) Dürr, H.; Kober, H.; Kausch, M. *Chem. Ber.* **1974**, *107*, 3415. Pauly, K.-H.; Dürr, H. *Tetrahedron Lett.* **1976**, 3649 and references cited therein.

(24) (a) Lenoir, D.; Lemmen, P. *Chem. Ber.* **1980**, *113*, 3112. (b) Gosnay, I.; Bergmann, E. O.; Robinovitz, M.; Agranat, I. *Isr. J. Chem.* **1972**, *10*, 423.

(25) (a) Gaspar, P. P.; Hsu, J.-P.; Chari, S.; Jones, M., Jr. *Tetrahedron* **1985**, *41*, 1479. (b) Brown, R. F. C. *Pyrolytic Method in Organic Chemistry*; Academic Press: New York, 1980; Chapter 5, pp 115–163. (c) Wentrup, C. In *Reactive Intermediates;* Abramovitch, R. A., Ed.; Plenum: New York, 1980; Vol. I, pp 263–320. (e) Jones, W. M. *Acc. Chem. Res.* **1977**, *10*, 353.

Scheme 8



became the major products (>70%) when **2d** was generated in C_6D_6. Furthermore, 1-*tert*-butyl FL (**2e**) produced only the intramolecular products **9e** and **10e**, no intermolecular reaction products with benzene being detected in this case (Table 3).

Reactions of 1-RFL in the Gas Phase at High Temperatures. Arylcarbenes generated in the gas phase at high temperatures are known to undergo carbene–carbene rearrangements of a complexity that rivals that of the rearrangements of carbocations in solution.[1,25] Reports of the gas phase reactions of carbenes have been largely concerned with substituted phenylcarbenes and diphenylcarbenes, probably because they usually undergo repeated rearrangement until they are trapped by a proximate reactive center to yield stable products that are often synthetically useful. In marked contrast, almost no reports of the gas phase reactions of fluorenylidene systems have appeared, presumably because similar rearrangement leading to useful products is not expected for FL due to the rigidity of the framework. However, recently we reported[26] the first example of a gas phase reaction of fluorenylidene that produces a significant product in fairly good yield; generation of 1-methoxyfluorenylidene (**19**) results in the formation of 1-phenanthrenol (**21**) most probably through initial formation of oxacyclopenta[*jk*]fluorene (**20**) by insertion of the carbene into the C–H bond of the methoxy group, followed by bond cleavage driven by the relief of ring strain in the initially formed product (Scheme 8). Isolation of the 1,2-dihydrocyclopenta[*jk*]fluorenes (e.g., **9**), even in fluid solution at ambient temperature, especially from FL bearing a bulky alkyl substituent at the 1-position prompted us to investigate the chemical behaviors of 1-alkyl FL in the high-temperature gas phase.

Flash vacuum pyrolysis (FVP, 350–450 °C, 10^{-4} Torr) of DAF (**1a**) and MeDAF (**1b**) resulted in the formation of mixtures consisting mainly of fluorenes (**3**) and fluorenones, no meaningful products being isolated in the mixture. This implies that FL does not undergo carbene–carbene rearrangement at least in the temperature ranges studied. This is not surprising since the reaction would be energetically highly unfavorable due to the planarity of the fluorenyl skeleton if the same types of intermediates were involved as in the habitual carbene–carbene rearrangements.[25] FVP of 1-ethyl-9-diazofluorene (**1c**), on the other hand, produced 1,2-dihydrocyclopentafluorene (**9c**)[19] in a fairly good yield as the sole isolable volatile product, obviously as a result of the intramolecular β-CH insertion in **2c** in the gas phase (Scheme 9). The formation of the high-energy molecule **9c**, which was not detected at all in solution reactions at room temperature, reflects the large amount of energy available in FVP and/or the simple fact that FVP favors unimolecular reactions. The exclusive formation of **9c** is however in contrast with that observed for **19**, where only the secondary rearranged product **21** is obtained under FVP conditions.[27]

FVP of **1d,e** resulted in the formation of the same intramolecular reaction products (**9** and **10**) as in the solution phase photolysis in benzene. A new intramolecular reaction product **9′** was also isolated. This was not detected in the photolytic mixtures (Scheme 9). The formation of **9** is again explicable in terms of direct C–H insertion of the carbenes into the β-CH bond at the 1-position, while those of **10** and **9′** are better explained by hydrogen atom abstraction to give **11** followed by the formal neophyl rearrangement to generate a new 1,5-biradical **13**. Appreciable formation of **9′** by intramolecular coupling of the rearranged biradical **13** in the gas phase pyrolytic reaction only may reflect the higher thermal energy under these conditions. In solution at room temperature, the biradical undergoes hydrogen migration to produce **10**, presumably because intramolecular coupling to give **9′** requires a higher activation energy due to the formation of the bent benzene ring.[19] In the low-pressure gas phase on the other hand, the biradical **13** will retain its excess energy carried over from preceding reaction steps, including the energy required to generate **2**, because collisional deactivation in the dilute gas phase is highly improbable.[28] Therefore, the intramolecular coupling to form **9′** can now compete with hydrogen migration to form **10**.

Inspection of the product yields in Scheme 9 immediately indicates that products derived from singlets and triplets, respectively, show considerable dependence on the substituents R and R′. The ratio of yields of **9**/(**9′** + **10**) is taken as the singlet/triplet ratio. The cyclization/rearrangement ratio **9′**/**10** also shows such dependence. It is seen that the ratio **9**/(**9′** + **10**) increases whereas the ratio **9′**/**10** decreases upon introduction of more methyl substituents. This can be explained in terms of the relative population of conformers in intermediates involved in the reactions (Scheme 10). Thus, in the nascent singlet carbene **2**, two rotational isomers, **A** and **B**, can be postulated. For **2e** (R = Me), these two isomers are identical and equally suitable for the intramolecular C–H insertion forming **9**, while in **2d** (R = H), conformer **B** not leading to **9** must be formed dominantly over **A** since, in the precursory diazomethane **1d**, the smallest substituent, i.e., H, must be located near the diazo functional group at the 9-position and also ^{1}**2dB** itself is energetically more stable than ^{1}**2dA**. Thus, ^{1}**2e** has a higher probability of undergoing C–H insertion to give **9e**, whereas ^{1}**2d** mainly decays to the triplet, ^{3}**2d**, in its dominant conformer **B**. In the triplet **2**, the carbene abstracts hydrogen to generate the biradical **11**. In **11e**, conformers **A** and **B** must be almost identical in terms of steric interaction between 1- and 9-substituents, while in **11d**, conformer **B** must be slightly favored over **A** because of interaction between the substituent R and the hydrogen atom in position 9. Thus, while **11A** can produce **9** by intramolecular coupling, if possible, the rearrangement to **13** seems the only pathway for **11B**. Assuming that the final products **9′** and **10** are derived from conformers **13A** and **13B**, respectively, the formation of **10** is statistically more favorable in **13e** than in **13d**, thus leading to a lower **9′**/**10** ratio.

This explanation implies, on the other hand, that the formation of **9c** on FVP of **1c** cannot be explained in terms of a simple

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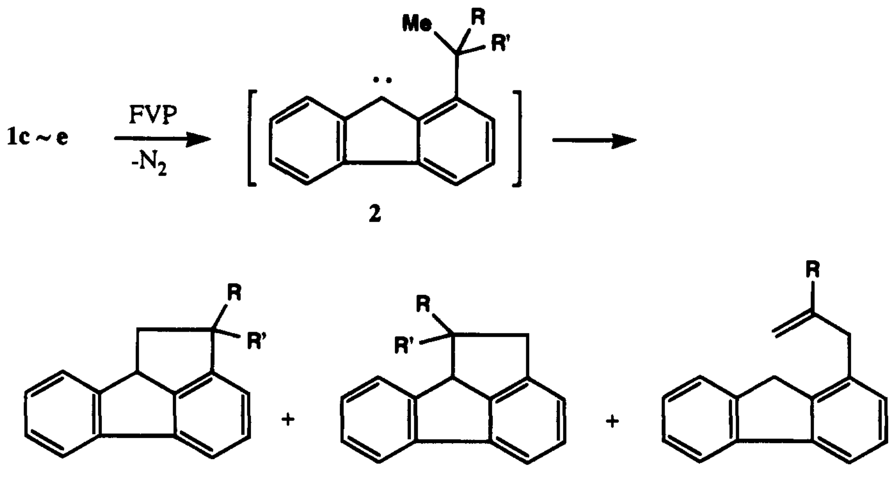
(26) Tomioka, H.; Kobayashi, N.; Ohtawa, Y.; Murata, S. *J. Org. Chem.* **1991**, *56*, 2609.

(27) From comparison of bond length [C–C (parafinic) = 1.537, C–O (alphatic ether) = 1.426 pm), bond angle [C–C–C (sp^2) = 110°, COC = 110°), and bond energy [CH_3–CH_3 = 88 kcal/mol, CH_3O–CH_3 = 80 kcal/mol), one would expect that **20** undergoes ring cleavage more easily than **9c**. Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972.

(28) Wentrup, C. *Reactive Molecules*; Wiley-Interscience: New York, 1984; p 162ff and references cited therein.

Scheme 9



	9	9'	10	9/(9'+10)	9'/10
c: R=R'=H	74%		—	—	—
d: R=H, R'=Me	9%	37%	12%	0.18	3.08
e: R=R'=Me	45%	17%	12%	1.55	1.42

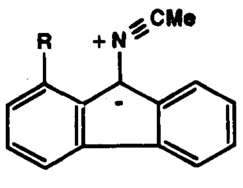
direct C−H insertion of singlet **2c** but can be better understood in terms of a stepwise reaction from the triplet state. Singlet **2c** should be less likely to be trapped by the β-C−H bonds than **2e** because of static reasons. Hence, **2c** should readily undergo isc to the triplet. In order to check this postulate, we generated **2c**-*d* labeled so as to discriminate between these two pathways. FVP of **2c**-*d* afforded a product, with the deuterium completely scrambled between positions 1 and 2; i.e., **9c**-*d* and **9'c**-*d* were formed in a roughly 1:1 ratio (Scheme 11). This is in agreement with the mechanism outlined in Scheme 10. Thus, taking into account a significant decrease in the yield of **9** on going from **1e** to **1d** and the essentially even distribution of deuterium in the cyclopentafluorenes **9c**, it is concluded that most of the singlet **2c** decays to the triplet faster than trapping of the singlet by the β-CH bonds. Thus, **9c** is produced mostly in a stepwise manner involving rearrangement from the triplet state.

Spectroscopic Studies. In order to obtain more insight into the intermediates involved in the reaction, the following spectroscopic studies were carried out using matrix isolation[29] and laser flash photolysis techniques.[30]

Irradiation ($\lambda > 300$ nm) of DAF (**1a**), matrix-isolated in Ar at 10 K, was monitored by UV−vis spectroscopy, which revealed a rapid disappearance of absorption bands due to **1a** (345.0, 336.5, 330.0, 289.5, 285.0, 280.0, 265.5, and 253.0 nm) and concomitant growth of new absorption bands at 464.0, 438.0, 324.0, 260.5, 257.0, 256.0, and 252.0 nm (Figure 1a,b). The carrier of the new bands was stable under these conditions, and no appreciable change occurred upon prolonged irradiation. Electronic absorption spectra of the parent triplet FL have been measured not only by irradiation in a 2-methyltetrahydrofuran matrix at 10 K but also by using picosecond laser flash photolysis at room temperature; it shows a strong absorption at 470 nm and a weaker one at ca. 440 nm.[2,30,31] We therefore assign the absorption observed in the matrix to ^{3}FL. Analogous irradiation of 1-Et- (**1c**) and 1-iPrDAF (**1d**) in Ar at 10 K also resulted in the formation of similar absorption bands, which are assigned to ^{3}1-EtFL (**2c**: 477.5, 449.5, 324.5, and 259.0 nm) and ^{3}1-iPrFL (**2d**: 479.0, 446.5, 324.5, and 255.5 nm), respectively.

Irradiation of tBuDAF (**1e**), however, produced completely different absorption spectra (Figure 1d), which showed no prominent set of bands around 470 and 450 nm but a very broad band near 455.0 nm along with strong and sharp bands at 301.5, 295.5, 289.5, and 263.5 nm. These product bands were stable at 10 K and changed very little upon further irradiation. These spectral features are obviously not in agreement with a substituted ^{3}FL and indicate that tBuFL (**2e**) is not stable under these conditions (Ar, 10 K). It is possible that the nascent **2e** immediately reacts with the *tert*-butyl group even at this low temperature. Alternatively, it may be that the precursor DFA (**1e**) in its electronically excited state reacts with the tBu group.[32]

Direct observations and kinetic studies of FL in solution at room temperature using laser flash photolysis (LFP) techniques indicate that the transient absorption ascribable to ^{3}FL exhibits a maximum at 470 nm and has a half-life of 17 ns in acetonitrile and that ^{3}FL undergoes two parallel reactions with acetonitrile, viz. H abstraction to give FLH$^\bullet$ (**6**, R = H), with an absorption maximum at 497 nm, and an electrophilic reaction to form ylide **22** (R = H), with an absorption band at 400 nm.[2,30,31]



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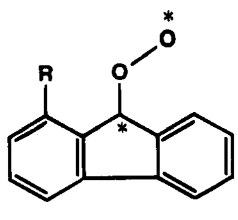

23

Flash photolysis of 1-EtDAF (**1c**, 4×10^{-4} M) in acetonitrile with a 10 ns pulse at 266 nm (fourth harmonic of a Nd/YAG

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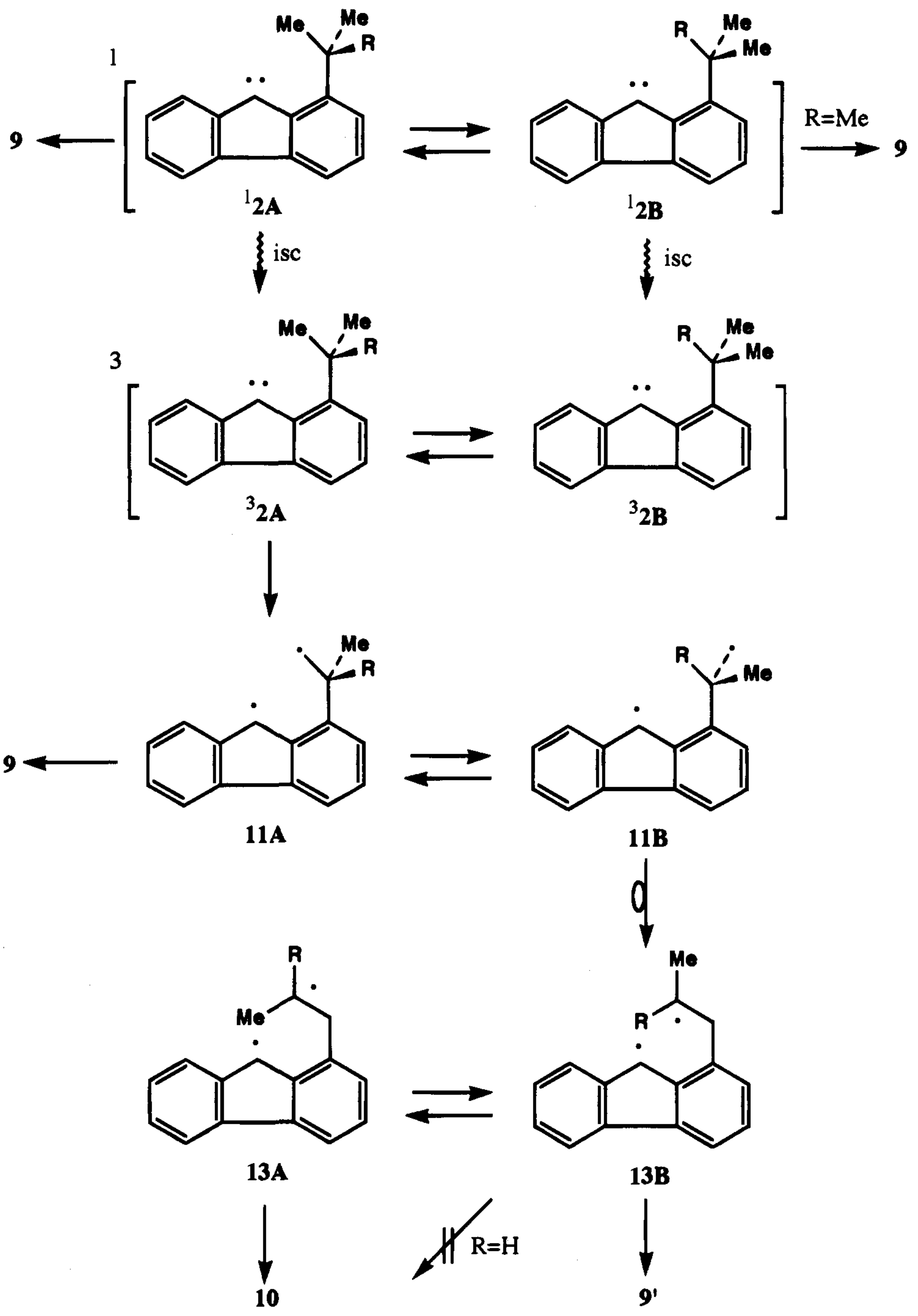
[29] For a review of carbenes studied in matrices, see: Sander, W.; Bucher, G.; Wierlacher, S. *Chem. Rev.* **1993**, *93*, 1583.

[30] For a review of carbenes studied by flash photolysis, see: Platz, M. S., Ed. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Plenum: New York, 1990.

[31] (a) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 5934. (b) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6631. (c) Griller, D.; Montgomery, C. R.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6813. (d) Griller, D.; Hadel, L.; Nazran, A. S.; Platz, M. S.; Wong, P. C.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2227.

Scheme 10



laser) resulted in the growth of an absorption band at 400 nm together with a weak band at 520 nm. These transient absorption bands had lifetimes of > 100 μs, but their decay rates were different. The half-life of the transient at 400 nm was 116 ± 10 μs, while that of 520 nm bands was 70 ± 10 μs (Figures 2 and 3). In analogy with the parent FL spectrum, we assigned the the 400 nm bands to ylide **22** (R = Et) and the weak bands at 520 nm to the radical FLH• (**6**, R = Et). This assignment is supported by similar flash photolysis of **1c** in cyclohexane, which produced only a 520 nm transient band at the expense of the 400 nm band. We were not able to detect any transient absorptions around 477.5 and 450 nm ascribable to ^{3}1-EtFL by our techniques. However, we could estimate the lifetime of **2c** from the first-order growth rate of **22c** at 400 nm as 38 ns. Essentially identical transient absorptions were observed on LFP of 1-iPrDAF (**1d**) in MeCN, where the transient band (520 nm) due to iPrFLH• (**6d**) was very weak. The formation of **22d** at 400 nm again followed first-order kinetics, with a lifetime of 33 ns.

LFP of tBuDAF (**1e**) gave completely different results. Thus, the photolysis resulted in the formation of a transient absorption

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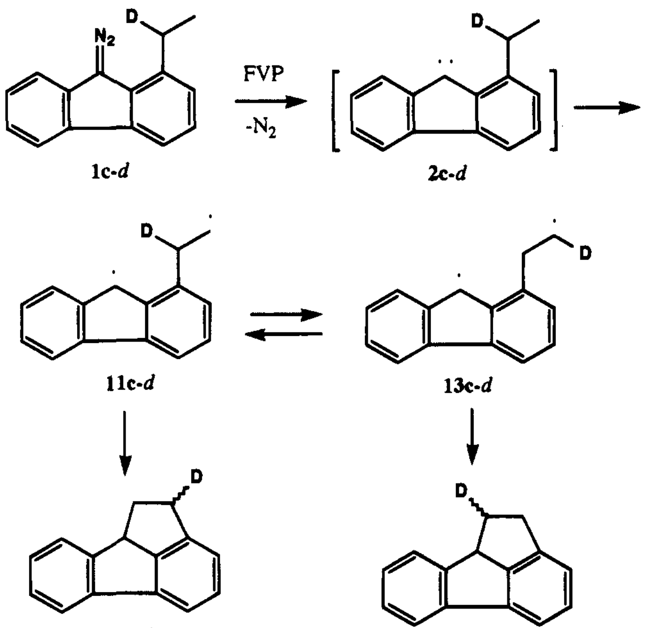
(32) Carbene chemists have for many years been concerned about precursor chemistry, and it has been shown that the diazo compounds used as sources of the carbene are possible for some of the observed chemistry. See for instance: (a) Chan, K.-T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082. (b) Lavilla, J. A.; Goodman, J. L. *Tetrahedron Lett.* **1990**, *31*, 5019. (c) Chambers, G. R.; Jones, M., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 4516. (d) Tomioka, H.; Kitagawa, H.; Izawa, Y. *J. Org. Chem.* **1979**, *44*, 3072. (e) Tomioka, H.; Okuno, H.; Izawa, Y. *J. Org. Chem.* **1980**, *45*, 5278. (f) Celebi, S.; Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 8613.

(33) If one assumes that the spectra of **11** and **13** should be similar to that of FLH• since the chromophore is virtually the same, the 370 nm band cannot be assigned to **11** or **13**, while **14** is a reasonable candidate. We thank a reviewer for pointing out this possibility.

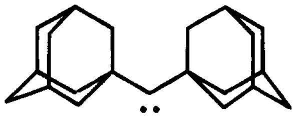
Scheme 11



at 370 nm, no other transient bands being observed. The formation of this band followed first-order kinetics, with a lifetime of 49 ns, and the decay was also found to be first order ($k = 9.2 \times 10^3\ s^{-1}$) (Figure 4). The transient absorption is ascribable to neither the ylide **22e** nor the radical **6e** and is also different from that observed on matrix photolysis. We tentatively assign this transient to intermediates generated from tBuFL as a result of reaction of the carbenic center with the *tert*-butyl group, e.g., **11**, **13**, and/or **14**.[33] The following control experiments support this assignment. First, essentially the same transient absorption was observed when LFP of **1e** was carried out in cyclohexane. This is in agreement with the result from product analysis that intramolecular products presumably by way of these intermediates, e.g., **11**, **12**, **13**, and/or **14**, dominate in this solvent. Second, LFP of **1e** in acetonitrile in the presence of 1,4-cyclohexadiene resulted in the generation of a transient product showing absorption at 520 nm at the expense of the 370 nm transient. Accepting that the 520 nm band is ascribable to tBuFLH• (**6e**), this observation is again in accord with the result of product studies, which had indicated that ^{3}tBuFL is quenched by the diene by hydrogen abstraction to form **4e**, presumably by way of **6e** (vide supra).[22] The rate constant for the reaction of tBuFL with the diene (0.05–0.27 M) was estimated to be $1.2 \times 10^8\ M^{-1}\ s^{-1}$ from investigation of the build-up kinetics at 520 nm as a function of the diene concentration in acetonitrile. Finally, LFP of **1e** in acetonitrile in the presence of oxygen produced a transient absorption at 450 nm again at the expense of the 370 nm absorption. The 450 nm transient is assigned to 1-*tert*-butylfluorenone oxide (**23**, R = tBu) since it is now well-documented that diarylcarbenes with triplet ground states are readily trapped by oxygen to give the corresponding diaryl ketone oxides which usually show a rather broad absorption band centered at 400–500 nm.[34] ^{3}FL (**2a**) itself is trapped by oxygen, for instance, with a rate constant of $(1.4 \pm 0.2) \times 10^9\ M^{-1}\ s^{-1}$ in Freon-113 to generate the fluorenone oxide absorption at 450 nm.[35] The rate constant for the reaction of tBuFL with oxygen (4×10^{-4} to ca. 3×10^{-3} M) was determined to be $(6.3 \pm 0.3) \times 10^9\ M^{-1}\ s^{-1}$.

Concluding Remarks

Effects of sterically congested groups on carbene reactivity have been noted occasionally in open chain systems. Two factors favoring triplet reaction are obvious. First, singlet reaction, which requires formation of two bonds simultaneously, will be disfavored relative to triplet reaction, which initially permits but one bond to form. Second, crowding around the carbene center should lead to widening of the central C–C–C angle toward a linear structure, which would strongly destabilize the singlet state; singlet-to-triplet isc therefore becomes very efficient. In diadamantylcarbene (**24**), for instance, the triplet is favored by a wider central angle as well as a decreased reactivity of the singlet, both for steric reasons; it therefore reacts with 2-butene in the triplet state to give diadamantylmethane as the major product.[36] Dimesitylcarbene (**25a**)[37] exhibits unique behavior owing to the expanded central C–C–C angle and the orthogonal orientation of the two aryl rings. Thus, in hydrocarbon solution at low temperature, this carbene does not react with the parent diazo compound to form azine but dimerizes to produce tetramesitylethylene, whereas for most other diarylcarbenes, azine formation and hydrogen abstraction are the dominant reaction pathways.[8d,37,38] Similar reactions are observed for (hexachlorodiphenyl)carbene (**25b**).[8a,b,37] (1,4-Diphenyltriazol-5-yl)carbene (**26a**), on other hand, reacts with benzene in an electrophilic manner in the singlet state to give the corresponding cycloheptatriene, while the corresponding phenylcarbene **26b** affords a mixture consisting principally of the symmetrical tetrasubstituted ethylene and the corresponding ethane, as a result of dimerization and abstraction of hydrogen by the triplet state, respectively.[39] This is again interpreted in terms of accelerated spin inversion induced by geometrical changes so as to forestall competing reaction by singlet **26b**.



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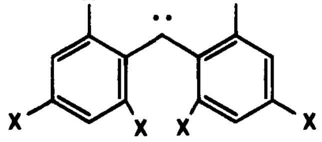
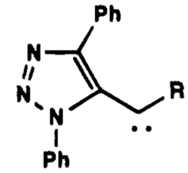


25a : X=Me
25b : X=Cl



26a : R=H
26b : R=Ph

It is reasonable to assume that the bond angle at the carbene center in FL is not changed significantly on introduction of bulky

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[34] (a) See for a review: Sander, W. W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344. (b) See also: Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Org. Chem.* **1989**, *54*, 1612.

[35] Casal, H. L.; Tanner, M.; Werstiuk, N. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 4616.

[36] Myers, D. R.; Senthilnathan, V. P.; Platz, M. S.; Jones, M., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 4232.

[37] Zimmerman, H. E.; Paskovich, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 2149.

[38] Nazran, A. S.; Lee, F. L.; Gabe, E. J.; Lepage, Y.; Northcott, D. J.; Park, J. M.; Griller, D. *J. Phys. Chem.* **1984**, *88*, 5251 and references cited therein.

[39] Smith, P. A. S.; Bruckmann, E. M. *J. Org. Chem.* **1974**, *39*, 1047.

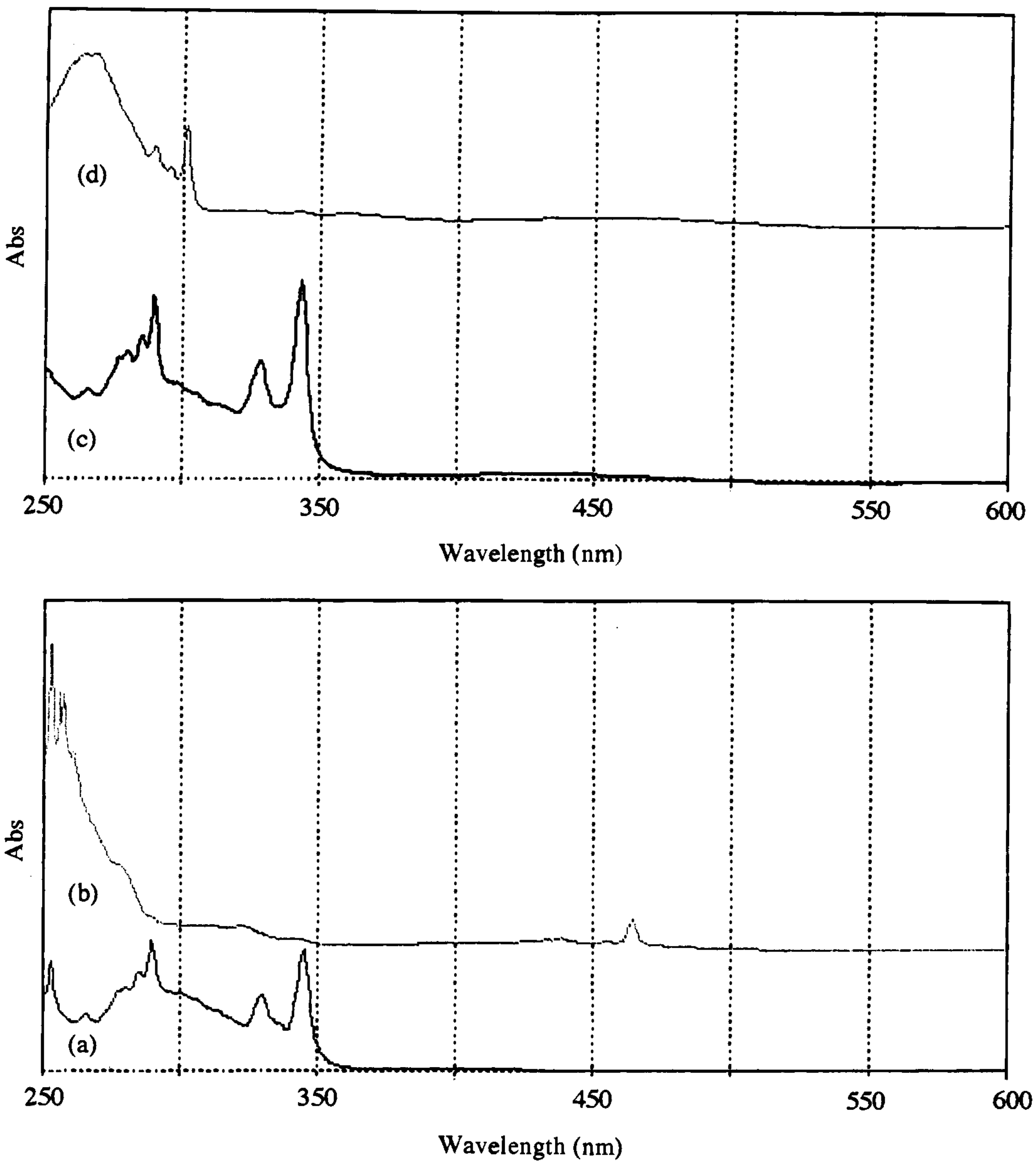

Figure 1. Photolysis of Diazofluorenes (**1**) in an Ar matrix at 10 K: (a) UV spectrum of **1a** in an Ar matrix at 10 K, (b) spectrum obtained after irradiation (λ > 300 nm), (c) UV spectrum of **1e** in an Ar matrix at 10 K, and (d) spectrum obtained after irradiation (λ > 300 nm).

groups at the 1-position because of the rigid structure. ΔG_{ST} will hardly change, and the singlet-to-triplet intersystem crossing efficiency is unaffected. ΔG_{ST} is also not altered significantly for electronic reasons when going from Me (σ_p -0.17) to tBu (σ_p -0.20). The present observations that triplet reactions gain over those of the singlet as more bulky substituents are introduced at the 1-position therefore suggest that the singlet–triplet reactivities are controllable to a significant extent simply by modulating the reaction rate of the singlet sterically.[40]

Reflecting the rigid carbene structure, the reaction patterns exhibited by sterically crowded ^{3}RFL are also unique. Thus, in the reaction with benzene, interaction of ^{1}RFL with the aromatic π-electrons is hindered by the 1-alkyl groups, and some of the singlets undergo isc to the triplets, which are forced to abstract hydrogen even from the aromatic solvent since dimerization of ^{3}RFL forming bis(1-alkylfluorenylidene) must also be energetically unfavorable. This is in sharp contrast to dimesitylcarbene, for which dimerization seems more favorable than hydrogen abstraction processes (see however the discussion of **28** below).[36,37]

The intramolecular reaction channels are also controlled by the geometrical factors imposed on the 1-alkylated FL. Thus, the concerted C–H insertion reaction of the singlet must involve the p orbital as well as σ orbital of the carbene. Interaction of the both orbitals with δ-C–H bonds through a triangular transition state is therefore geometrically highly unfavorable. Abstraction of the δ-hydrogen involving the half-filled, in-plane σ orbital of the triplet carbene, on the other hand, can proceed much more easily by way of a six-membered transition state. During the course of this study, Kirmse and co-workers have shown that intramolecular C–H insertion reactions of monophenylcarbenes (**27**) bearing 2-alkoxy substituents to form five-membered rings proceed by way of a triplet abstraction–recombination mechanism. The concerted singlet mechanism is restored for intramolecular C–H insertion reactions leading to six-membered rings.[41] This is taken to indicate that the

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[40] It appears that the spin-state equilibration of arylcarbenes is faster than (or competitive with) chemical reactions. This is especially so with FL, which has a small ΔG_{ST}. Supposing that ΔG_{ST} and S-T intersystem crossing efficiencies are not be significantly altered by introduction of alkyl group at the 1-position, steric hindrance affects the reactions of the singlet in equilibrium with the triplet.

[41] Kirmse, W.; Özkir, I. S. *J. Am. Chem. Soc.* **1992**, *114*, 7590. Kirmse, W.; Özkir, I. S.; Schnitzler, D. *J. Am. Chem. Soc.* **1993**, *115*, 792. See also: Kirmse, W.; Hömberger, G. *J. Am. Chem. Soc.* **1991**, *113*, 3925.

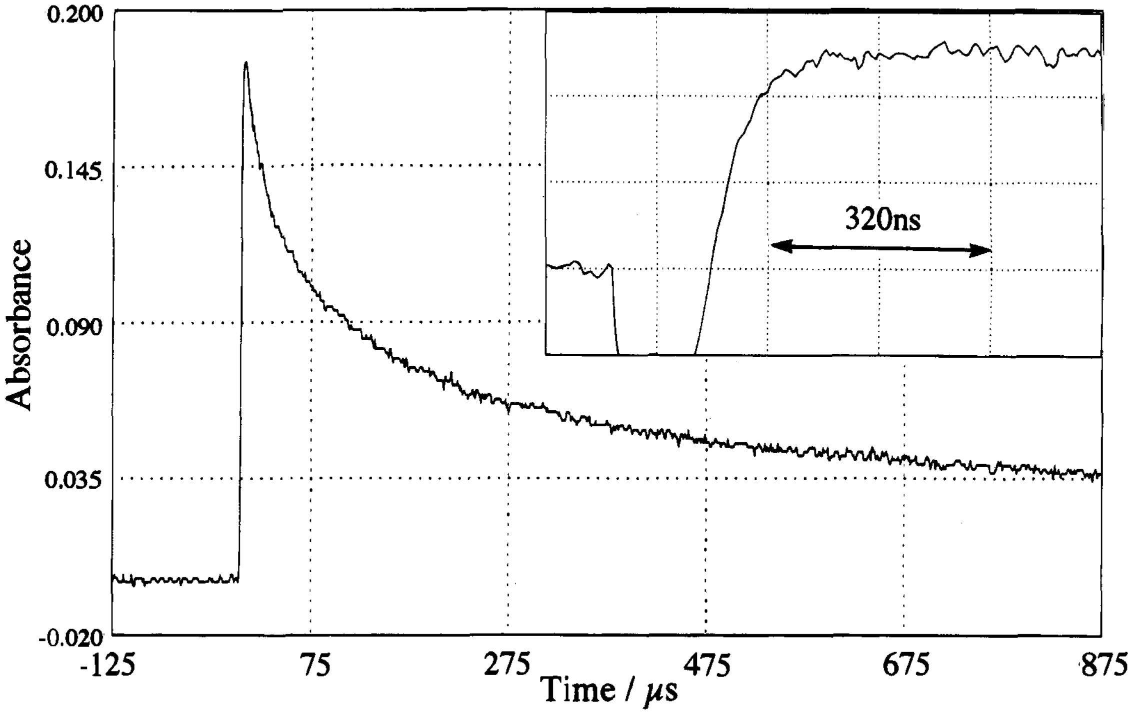

Figure 2. Growth and decay of the transient absorption monitored at 400 nm in LFP of 1-EtDAF (**1c**) in acetonitrile.

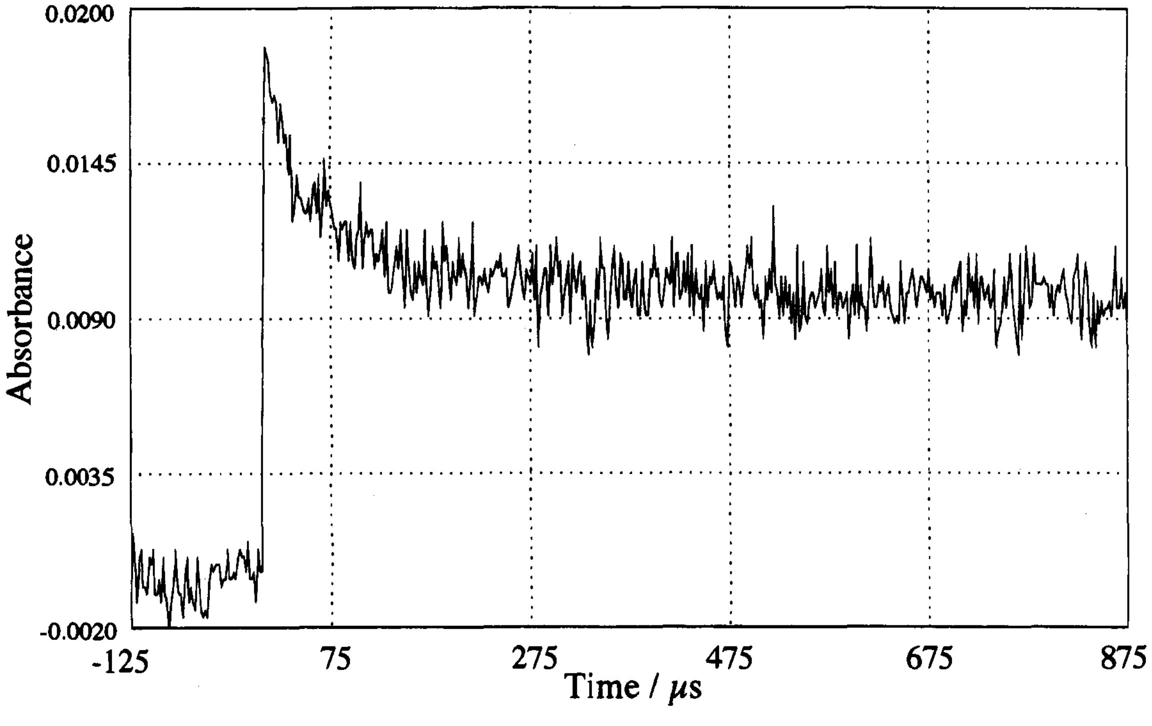

Figure 3. Decay of the transient absorption monitored at 520 nm in LFP of 1-EtDAF (**1c**) in acetonitrile.

interaction of both orbitals in the singlet carbene with δ-C−H bonds is accompanied by rotation of the bond connecting the divalent carbon to the benzene ring, with concomitant loss of benzylic reasonance stabilization[42] and deformation of bond angles. In contrast, the transfer of δ-hydrogen to the σ orbital of the triplet carbene can proceed by way of a six-membered transition state.[41]

A unique behavior observed in the intramolecular reaction of RFL is that triplet reactions always involve rearrangement. Intramolecular δ-H abstraction of (2-alkoxyphenyl)carbene (**27**), for instance, leads to almost exclusive formation of 2,3-dihydrobenzofurans by way of 1,5-biradicals.[42] (2,4,6-Tri-*tert*-butylphenyl)phenylcarbene (**28**), a diphenylcarbene analogue of *tert*-butyl FL (**2e**), also quantitatively produces 4,6-di-*tert*-butyl-1,1-dimethyl-3-phenylindan via the triplet state.[8c] The formation of quite a variety of rearranged products from triplet RFL not only in fluid solution but also in the gas phase is rather uncommon in arylcarbene chemistry and is explained in terms of the ring strain imposed on the rigid fluorenylidene structure.

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[42] Kirmse, W.; Kund, K.; Ritzer, E.; Dorigo, A. E.; Houk, K. N. *J. Am. Chem. Soc.* **1986**, *108*, 6045. Hömberger, G.; Dorigo, A. E.; Kirmse, E.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 475.

[43] Bogert, M. T.; Gortner, R. A.; Amend, C. G. *J. Am. Chem. Soc.* **1911**, *33*, 951.

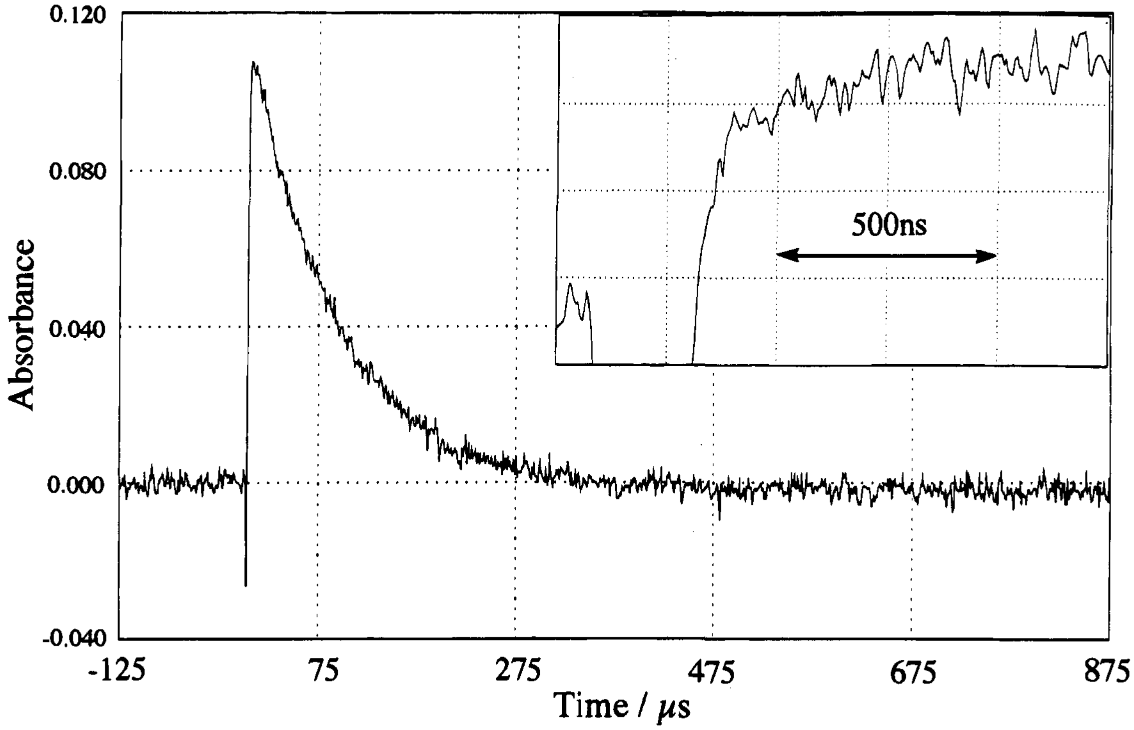
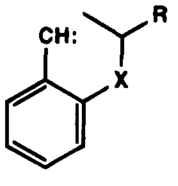
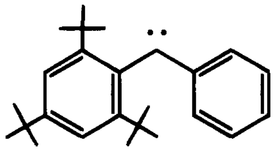


Figure 4. Growth and decay of the transient absorption monitored at 370 nm in LFP of 1-tBuDAF (**1e**) in acetonitrile.



27 X=CH$_2$, O



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The intervening 1,5-diradicals undergo the slow neophyl rearrangement competitively with ring closure since 1,5-cyclization is retarded by the strain of the resulting cyclopentafluorenes.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on JEOL JNM-100 and JNM-EX-270 spectrometers. IR spectra were measured on JASCO A-100 and IR-700 spectrometers, and UV–vis spectra were recorded on a Hitachi 220S spectrophotometer. GC–MS spectra were recorded on a Shimadzu QP-1000 mass spectrometer with a GC column prepared from 5% Silicone OV-17 on Diasolid L (5.0 mm x 1.0 m). The GC analyses were performed on a Yanagimoto instrument, Model G-80. The GC column was prepared from 5% Silicone OV-17 on Diasolid L (5.0 mm x 1.0 m) or 5% PEG-20M on Diasolid L (5.0 mm x 1.0 m). Gel permeation liquid chromatography was carried out on a JASCO HLC-01 high-pressure liquid chromatograph equipped with a Shodex GPG H-2001 column. Thin layer chromatography was carried out on a Merck Kieselgel 60 PF$_{254}$, and column chromatography was performed on a Fuji Davison silica gel BW-127ZH or ICN alumina (neutral, activity I).

Materials. Preparation of 2-Amino-2′-alkylbenzophenone: General Procedure.[9] To a vigorously stirred solution of 2-methyl-3,1-benzoxaz-4-one[43] (0.125 mol) in anhydrous benzene (250 mL) at 0 °C was added gradually (2 h) 2-alkylbenzene magnesium bromide (formed from 0.125 mol of 2-alkylbromobenzene and 0.130 mol of Mg) in anhydrous Et$_2$O (85 mL). After the mixture was stirred overnight at room temperature, it was treated with saturated ammonium chloride solution and extracted with Et$_2$O. The extract was dried (Na$_2$SO$_4$) and evaporated to leave 2-(acetylamino)-2′-alkyl-benzophenone as a pale yellow solid. The (acetylamino)benzophenone thus obtained (0.06 mol) was hydrolyzed by heating in ethanol (120 mL) containing concentrated hydrochloric acid (20 mL) for 4 h, and the mixture was made alkaline with aqueous ammonia to produce 2-amino-2′-alkyl-benzophenone. 2-Isopropylbromobenzene[44] and 2-*tert*-butylbromobenzene[44] were prepared according to the literature procedures.

2-Amino-2′-methylbenzophenone: 47%; mp 83–84 °C (lit.[9] 84%); ^{1}H NMR (CDCl$_3$) δ 2.28 (s, 3H), 6.55 (dd, J = 8.0, 7.3 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 7.12–7.48 (m, 6H).

2-Amino-2′-ethylbenzophenone: 75%; brown liquid (crude); ^{1}H NMR (CDCl$_3$) δ 1.22 (t, J = 8.0 Hz, 3H), 2.60 (q, J = 8.0 Hz, 2H), 6.46 (dd, J = 8.1, 8.3 Hz, 1H), 6.64 (dd, J = 8.1, 8.0 Hz, 1H), 6.78–7.42 (m, 6H).

2-Amino-2′-isopropylbenzophenone: 58%; mp 128–130 °C; ^{1}H NMR (CDCl$_3$) δ 1.18 (d, J = 7.0 Hz, 6H), 2.94 (sept, J = 7.2 Hz, 1H), 6.36 (dd, J = 8.2, 8.3 Hz, 1H), 6.52 (dd, J = 8.2, 8.1 Hz, 1H), 6.63–7.36 (m, 6H).

2-Amino-2′-*tert*-butylbenzophenone: 26%; mp 93–95 °C; ^{1}H NMR (CDCl$_3$) δ 1.33 (s, 9H), 6.20 (bs, 2H), 6.28–6.64 (m, 2H), 6.80–7.56 (m, 6H).

Preparation of 1-Alkyl-9-fluorenone: General Procedure.[9] To a vigorously stirred solution of 2-amino-2′-alkylbenzophenone (0.027 mol) in 5 N HCl (80 mL) at 0 °C was added sodium nitrite (0.032 mol) in water (25 mL) slowly (10 min). The mixture was gradually heated to reflux and then refluxed for 2.5 h. After the mixture was cooled and extracted with Et$_2$O, the extract was washed repeatedly with 5% KOH and water. After drying, evaporation of the solvent afforded the desired fluorenone.

1-Methyl-9-fluorenone: 60%, mp 98–99 °C (lit.[9] 98 °C); ^{1}H NMR (CDCl$_3$) δ 2.54 (s, 3H), 6.80–6.98 (m, 1H), 7.00–7.24 (m, 3H), 7.24–7.38 (m, 2H), 7.45 (d, J = 7.1 Hz, 1H); MS *m/e* (relative intensity) 194 (M$^+$, 100), 165 (90.2), 82 (30.5).

1-Ethyl-9-fluorenone: 49%; mp 91–93 °C; ^{1}H NMR (CDCl$_3$) δ 1.25 (t, J = 8.0 Hz, 3H), 3.05 (q, J = 8.0 Hz, 2H), 6.90–7.10 (m, 1H), 7.10–7.32 (m, 3H), 7.32–7.46 (m, 2H), 7.54 (d, J = 7.2 Hz, 1H); MS *m/e* (relative intensity) 208 (M$^+$, 100), 193 (40.2), 178 (30.2), 165 (35.3), 152 (20.0).

1-Isopropyl-9-fluorenone: 46%; mp 62–64 °C (lit.[45] 63–65 °C); ^{1}H NMR (CDCl$_3$) δ 1.18 (d, J = 7.2 Hz, 6H), 2.94 (sept, J = 7.2 Hz, 1H), 6.36 (dd, J = 8.2, 8.4 Hz, 1H), 6.52 (dd, J = 8.2, 8.0 Hz, 1H),

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[44] Crawford, M.; Stewart, F. H. C. *J. Chem. Soc.* **1952**, 4443.

[45] Mukai, T.; Tsurata, H.; Nozoe, T. *Nippon Kagaku Kaishi* **1968**, 991.

6.63−7.36 (m, 5H); MS *m/e* (relative intensity) 222 (M^+, 90.2), 207 (100), 194 (65.2), 178 (47.3).

1-*tert*-Butyl-9-fluorenone: 66%; yellow oil (crude); ^{1}H NMR ($CDCl_3$) δ 1.46 (s, 9H), 7.06−7.56 (m, 7H); MS *m/e* (relative intensity) 236 (M^+, 60.0), 221 (45.2), 207 (25.0), 194 (100).

Preparation of 1-Alkyl-9-diazofluorene (1b−d): General Procedure. A solution of 1-alkyl-9-fluorenone (10 mmol), hydrazine hydrate (20 mmol), and hydrazine hydrochloride (10 mmol) in anhydrous ethanol (50 mL) was placed in a round-bottom flask, and the whole system was deaerated by repeated cycles of evacuation and purge with argon. This deaeration process was essential in order to obtain pure hydrazone in higher yield. The mixture was refluxed under an atmosphere of argon until a TLC monitor showed that most of the ketone was consumed. After cooling, the solvent was evaporated and the mixture was added to Et_2O. The ethereal layer was washed with water, dried (Na_2SO_4), and evaporated. The crude hydrazone containing some fluorenone and fluorenol was purified by column chromatography (silica gel, *n*-hexane−$CHCl_3$).

The purified hydrazone (1 mmol), anhydrous ether (15 mL), anhydrous sodium sulfate (300 mg), MnO_2 on SiO_2 (10 mmol), and saturated ethanolic potassium hydroxide (0.2 mL) were placed in a round-bottom flask, and the mixture was stirred in the dark room for 10 h. After filtration, the solvent was removed on a rotary evaporator to afford essentially a quantitative yield of the crude diazo compound. The crude material was purified by the use of gel permeation liquid chromatography with $CHCl_3$ as an eluent. MnO_2 on SiO_2 was prepared as follows. To a solution of $KMnO_4$ (3.79 g, 0.024 mol) in H_2O (60 mL) was added silica gel (Merck, 70−230 mesh, 60 g) and H_2O was evaporated at 60 °C under reduced pressure. The resulting brown powder was added to a vigorously stirred solution of $MnSO_4{\cdot}4{-}5H_2O$ (9.3 g) in H_2O (100 mL) and the mixture was stirred for 1 h. The dark brown solid was filtered, washed with H_2O, and dried at 55−60 °C in vacuo.

1-Methyl-9-diazofluorene (1b): mp 66−68 °C; ^{1}H NMR ($CDCl_3$) δ 2.54 (s, 3H), 6.92−7.50 (m, 5H), 7.50−7.96 (2H); IR (KBr) 2060 cm^{-1}.

1-Ethyl-9-diazofluorene (1c): mp 73−74 °C; ^{1}H NMR ($CDCl_3$) δ 1.31 (t, J = 8.2 Hz, 3H), 2.86 (q, J = 8.2 Hz, 2H), 7.00−7.48 (m, 5H), 7.67−7.92 (m, 2H); IR (KBr) 2060 cm^{-1}.

1-Isopropyl-9-diazofluorene (1d): mp 78−80 °C; ^{1}H NMR ($CDCl_3$) δ 1.32 (d, J = 7.2 Hz, 6H), 3.21 (sept, J = 7.2 Hz, 1H), 7.11−7.40 (m, 5H), 7.66−7.95 (m, 2H); IR (KBr) 2060 cm^{-1}.

Preparation of 1-*tert*-Butyl-9-diazofluorene (1e). To a stirred solution of 1-*tert*-butyl-9-fluorenone (10 mmol) in anhydrous ethanol (20 mL) was added $NaBH_4$ (3 mmol), and the mixture was refluxed for 2 h. Usual workup, followed by column chromatography (silica gel, *n*-hexane−$CHCl_3$) afforded 1-*tert*-butyl-9-fluorenol as a brownish oil in 52% yield: ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 9 H), 5.88 (d, J = 8.1 Hz, 1H), 7.18−7.66 (m, 7H). The fluorenol (0.87 mmol) was added to a cooled solution of freshly distilled PBr_3 (0.31 mmol) in dry pyridine (4.2 mL) at 0 °C, and the mixture was stirred for 1 h at 0 °C and then overnight at room temperature. The mixture was added to ether−water, and the ethereal layer was washed with water. Drying and evaporation of the solvent produced crude 1-*tert*-butyl-9-bromofluorene as a brown oil: 98%; ^{1}H NMR ($CDCl_3$) δ 1.58 (5.9H), 6.28 (s, 1H), 7.17−7.67 (m, 7H).

To a stirred mixture of ethyl carbamate (8.3 mmol) and $AgBF_4$ (1.10 mmol) in anhydrous dioxane (5 mL) heated at 90 °C was added the bromofluorene (0.83 mmol) in 1 mL of dioxane, and the mixture was refluxed for 1.5 h. After the mixture was cooled and filtered, the filtrate was washed well with $CHCl_3$ and water. Drying and concentration of the organic layer gave an oily solid which was subjected to short-path distillation to produce ethyl *N*-(1-*tert*-butyl-9-fluorenyl)carbamate as a brownish solid: 86%; mp 155−157 °C; ^{1}H NMR ($CDCl_3$) δ 1.24 (q, J = 7.2 Hz, 3H), 1.47 (s, 9H), 4.19 (q, J = 7.2 Hz, 2H), 4.72 (d, J = 10.1 Hz, 1H), 6.13 (d, J = 10.1 Hz), 7.15−7.74 (m, 7H).

To a stirred and cooled solution of the carbamate (0.62 mmol) in acetic acid (1.24 mL) and acetic anhydride (6.2 mL) at 0 °C was added a 60 mg portion of $NaNO_2$ (total 930 mg, 13.6 mmol) every 20 min for 5 h. The mixture was stirred overnight at 10 °C, poured into ice−water, and extracted with ether. The ethereal layer was washed with water, 5% Na_2CO_3, and water and dried. Evaporation of the solvent afforded ethyl *N*-nitroso-*N*-(1-*tert*-butyl-9-fluorenyl)carbamate as brown oil: 80%; ^{1}H NMR ($CDCl_3$) δ 1.13 (t, J = 7.3 Hz, 3H), 1.25 (s, 9H), 3.37 (q, J = 7.3 Hz, 2H), 3.92−4.16 (m, 1H), 6.93−7.62 (m, 7H).

To a heated and deaerated solution of potassium *tert*-butoxide (1.5 mmol) in *tert*-butyl alcohol (5 mL) at 60 °C was added a solution of the nitrosocarbamate (0.50 mmol) in *tert*-butyl alcohol (15 mL) at once under an atmosphere of argon. The mixture was stirred for 1 h at 60 °C and poured into ice−water. The mixture was extracted with Et_2O, and the ethereal layer was dried and then evaporated to leave crude 1-*tert*-butyl-9-diazofluorene (**1e**) as purple solid. The crude material was purified by column chromatography (neutral alumina, *n*-hexane) at 0 °C, followed by gel permeation chromatography ($CHCl_3$): mp79−80 °C; ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 9H), 7.16−7.56 (m, 5H), 7.55−8.04 (m, 2H); IR (KBr) 2060 cm^{-1}.

Irradiation for Product Identification. In a typical run, a solution of the diazofluorenes (ca. 50 mg) in solvents (5 mL) was placed in a Pyrex tube of 10 mL capacity and irradiated with a high-pressure, 300 W mercury lamp at 10 °C until all the diazo compound was destroyed. The irradiation mixture was then concentrated on a rotary evaporator below 20 °C. Individual components were isolated either by column chromatography or by preparative TLC and identified by NMR and MS. These fully characterized products were then used as "authentic" compounds for product identification by coinjection in GC−MS.

Irradiation of **1** in methanol was carried out as described above, and the following methyl ethers (**3**) were isolated almost quantitatively.

1-Methyl-9-methoxyfluorene (3b): ^{1}H NMR ($CDCl_3$) δ 2.54 (s, 3H), 2.79 (s, 3H), 5.40 (s, 1H), 6.72−7.45 (m, 7H); MS *m/e* (relative intensities) 210 (M^+, 30.1), 195 (100), 193 (15.2), 165 (38.2).

1-Ethyl-9-methoxyfluorene (3c): ^{1}H NMR ($CDCl_3$) δ 1.25 (t, J = 8.2 Hz, 3H), 2.77 (s, 3H), 2.67 (q, J = 8.2 Hz, 2H), 5.47 (s, 1H), 6.73-7.40 (m, 7H); MS *m/e* (relative intensity) 224 (M^+, 28.1), 195 (100), 193 (25.3), 128 (30.8), 165 (36.5).

1-Isopropyl-9-methoxyfluorene (3d): ^{1}H NMR ($CDCl_3$) δ 1.28 (d, J = 7.2 Hz, 6H), 2.85 (s, 3H), 351 (sept, J = 7.2 Hz, 1H), 5.65 (s, 1H), 7.00−7.55 (m, 7H); MS *m/e* (relative intensity) 238 (M^+, 28.5), 206(22.3), 195 (100), 191 (20.1), 165 (31.4).

1-*tert*-Butyl-9-methoxyfluorene (3e): ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 9H), 2.80 (s, 3H), 5.95 (s, 1H), 7.16−7.66 (m, 7H). MS *m/e* (relative intensity) 252 (M^+, 27.3), 221 (16.6), 206 (23.2), 195 (100), 165 (24.1).

Irradiation of **1** in cyclohexane produced the following products.

1-Methyl-9-cyclohexylfluorene (7b): ^{1}H NMR ($CDCl_3$) δ 0.61−2.41 (m, 1H), 2.60 (s, 3H), 4.05 (d, J = 2.3 Hz, 1H), 7.10−7.54 (m, 4H), 7.55-7.78 (m, 3H); MS *m/e* (relative intensity) 262 (M^+, 30.1), 180 (100), 165 (23.5).

1-Ethyl-9-cyclohexylfluorene (7c): ^{1}H NMR ($CDCl_3$) δ 0.60−2.39 (m, 11H), 1.31 (t, J = 7.1 Hz, 3H), 2.82 (q, J = 7.1 Hz, 2H), 4.00 (d, J = 2.3 Hz, 1H), 7.00−7.40 (m, 4H), 7.44−7.74 (m, 3H); MS *m/e* (relative intensity) 276 (M^+, 39.2), 194 (100), 179 (20.3), 178 (33.6), 165 (42.1).

1-Isopropyl-9-cyclohexylfluorene (7d): ^{1}H NMR ($CDCl_3$) δ 0.55−2.15 (m, 11H), 1.25 (d, J = 6.5 Hz, 6H), 3.17 (sept, J = 6.5 Hz, 1H), 3.88 (d, J = 2.1 Hz, 1H), 6.82−7.13 (m, 4H), 7.15−7.48 (m, 3H); MS *m/e* (relative intensity) 290 (M^+, 70.7), 247 (15.8), 208 (100), 192 (42.1), 179 (19.6), 165 (99.2).

1,1′-Dimethyl-9,9′-bifluorenyl (5b): ^{1}H NMR ($CDCl_3$) δ 2.91 (s, 6H), 5.04 (s, 2H), 5.88 (d, J = 8.0 Hz, 2H), 6.64 (dd, J = 8.0, 7.0 Hz, 2H), 6.96 (dd, J = 8.0, 7.0 Hz, 2H), 7.06−7.80 (m, 8H). *meso*-Isomer: 2.85 (s, 6H), 4.94 (s, 2H), 6.80−7.80 (m, 14H); MS *m/e* (relative intensity) 360 (M^+, 8.5), 180 (19.1), 179 (100), 78 (89.3).

1,1′-Diethyl-9,9′-bifluorenyl (5c). *dl*-Isomer: ^{1}H NMR ($CDCl_3$) δ 1.52 (t, J = 7.6 Hz, 6H), 3.24 (q, J = 7.6 Hz, 4H), 5.03 (s, 2H), 5.87 (d, J = 7.5 Hz, 2H), 6.64 (dd, J = 7.5, 7.3HZ, 2H), 6.98 (dd, J = 7.5, 7.3 Hz, 2H), 7.14−7.62 (m, 8H). *meso*-Isomer: ^{1}H NMR ($CDCl_3$) δ 1.10 (bs, 6H), 2.40 (bs, 4H), 4.97 (s, 2H), 6.88−7.62 (m, 14H); MS *m/e* (relative intensity) 386 (M^+, 87.4), 194 (15.9), 193 (100), 178 (31.9), 165 (10.2).

1,1′-Diisopropyl-9,9′-bifluorenyl (5d). *dl*-Isomer: ^{1}H NMR ($CDCl_3$) δ 1.53 (d, J = 7.7 Hz, 12H), 3.81 (sept, J = 7.7 Hz, 2H), 4.98 (s, 2H), 5.81 (d, J = 8.0, 7.0 Hz, 2H), 6.93 (dd, J = 8.0, 7.0 Hz, 2H), 7.19−7.53 (m, 8H). *meso*-Isomer: ^{1}H NMR ($CDCL_3$) δ 1.02 (bs, 12H), 3.89 (bs, 2H), 4.93 (s, 2H), 6.80−7.53 (m, 14H). MS *m/e* (relative intensity) 414 (M^+, 7.4), 208 (17.0), 207 (100), 192 (25.5), 191 (12.7), 165 (12.7).

Irradiation of **1d** with α-methylstyrene afforded the following cyclopropane.

2-Phenyl-2-methyl-1′-isopropylspiro[cyclopropane-1,9′-fluorene] (8d). Ph-iPr *anti*-isomer: ^{1}H NMR (CDCl$_3$) δ 1.13 (d, J = 6.2 Hz, 3H), 1.46 (d, J = 6.6 Hz, 3H), 1.68 (s, 3H), 2.46 (d, J = 6.6 Hz, 1H), 2.66 (d, J = 6.6 Hz, 1H), 3.48 (sept, J = 6.6 Hz, 1H), 5.85 (d, J = 6.2 Hz, 1H), 6.30 (bs, 1H), 6.90−7.84 (m, 5H), Ph-iPr *syn*-isomer: ^{1}H NMR (CDCl$_3$) δ 0.31 (d, J = 6.6 Hz, 3H), 0.81 (d, J = 6.6 Hz, 3H), 1.51 (s, 3H), 2.17 (d, J = 6.2 Hz, 1H), 2.39 (sept, J = 6.6 Hz, 1H), 2.78 (d, J = 6.6 Hz, 1H, 6.30 (bs, 1H), 6.90−7.84 (m, 6H); HRMS calcd for $C_{25}H_{24}$ 324.1878, found 324.1865.

Irradiation of **1d** with (*E*)-α-methyl-*β*-deuteriostyrene afforded **8d**-*d* as a mixture of *syn*- and *anti*-isomers. The ^{1}H NMR spectrum is the same as that of the non-deuterated cyclopropane except that the cyclopropyl protons are two sets of two singlets, i.e., δ 2.17, 2.78 and δ 2.46, 2.66, ascribable to *syn*- and *anti*-isomers, respectively. The ^{1}H NMR resonances of unreacted (*E*)-α-methyl-*β*-deuteriostyrene show that no isomerization of the olefin occurred under the experimental conditions.

Irradiation of **1** in benzene afforded the following benzene adducts.

4-Methyl-5*H*- and 7*H*-benzocycloheptene (16b and 17b): ^{1}H NMR (CDCl$_3$) δ 2.60 (s, 3H), 2.32 (d, J = 7.0 Hz), 3.22 (d, J = 7.0 Hz), 5.6−6.5 (m, 4H), 7.1−8.6 (m, 7H); MS *m/e* (relative intensity) 256 (M$^+$, 85.1), 254 (24.3), 241 (100), 239 (58.5), 120 (44.9).

4-Ethyl-5*H*- and 7*H*-benzocycloheptene (16c and 17c): ^{1}H NMR (CDCl$_3$) δ 1.30 (t, J = 8.2 Hz, 3H), 2.28 (d, J = 7.5 Hz), 2.76 (q, J = 8.2 Hz, 2H), 3.20 (d, J = 7.5 Hz), 5.6−6.3 (m, 4H), 7.00−7.48 (m, 7H); MS *m/e* (relative intensity) 270 (M$^+$, 72.3), 255 (65.9), 241 (100), 239 (65.9), 120 (37.2).

4-Isopropyl-5*H*- and 7*H*-benzocycloheptene (16d and 17d): ^{1}H NMR (CDCl$_3$) δ 1.30 (d, J = 7.5 Hz, 6H), 2.20 (d, J = 7.3 Hz), 3.24 (d, J = 7.0 Hz), 3.20 (sept, J = 7.5 Hz, 1H), 3.5−6.4 (m, 4H), 6.28−8.60 (m, 7H); MS *m/e* (relative intensity) 284 (M$^+$, 5.3), 241 (22.3), 207 (27.6), 178 (15.9), 165 (58.0), 77 (100).

Irradiation for Analytical Purposes. All irradiations outlined in Tables 1−3 were carried out in a Pyrex tube of 5.0 mL capacity. In order to avoid ambiguity in relative yields due to oxidation, the solution was degassed by subjecting the sample to a minimum of three freeze−degas−thaw cycles at a pressure near 10^{-5} Torr before irradiation and the tube was sealed under reduced pressure. Irradiation was carried out with a filtered light from the mercury lamp through a Corning CS-052 filter and generally continued until all the diazo compound was consumed. Product identifications were established either by GC or by GC−MS comparison with authentic samples separated as described above, and product distributions were conveniently determined by standard GC techniques. The competition experiments were carried out by irradiating the precursor diazomethane **1** in a degassed binary mixture of two substrates. Product ratios were determined by GC with a calibrated flame ionization detector. Experiments were duplicated, and average deviations from the mean values were <3%.

Flash Vacuum Pyrolysis. The apparatus used for the FVP consisted of a vertical quartz tube (30 mm i.d. × 35 cm long) maintained at the desired temperature by using a resistance wire. The tube was fitted with a loose plug of quartz wool 10 cm below the top of the heated zone. At the top of the tube, provision was made for the introduction of solid reactants via a solid addition tube. The lower end of the pyrolysis tube was fitted with consecutive U-tubes immersed in liquid nitrogen. The pyrolysis tube was bent near the bottom such that the pyrolysis zone was angled about 35° from vertical.

In a typical experiment, ca. 1 mmol of the diazo compound was dissolved in pentane, quartz powder (ca. 1 mL) was added, and the pentane was removed under reduced pressure, leaving the diazoalkane coated on the support. The sample was then placed in the solid addition tube and continuously added from the top of the tube at an operating pressure of 10^{-5} Torr. The volatile products were collected in a trap cooled with liquid nitrogen and chromatographed by preparative TLC on silica gel. For analytical runs, the sample was washed out of the trap with acetone, the resulting solution was diluted to 5.0 mL, and an internal standard was added for GC analysis.

FVP of **1c** was carried out as described above, and the following products were isolated.

1,2-Dihydrocyclopentafluorene (9c): ^{1}H NMR (CDCl$_3$) δ 1.53−1.96 (m, 1H), 2.56−3.03 (m, 2H), 3.29−3.73 (m, 1H), 4.09 (dd, J = 9.1, 9.0 Hz, 1H), 6.77−7.52 (m, 7H); MS *m/e* (relative intensity) 192 (M$^+$, 100), 1.65 (45.7), 84 (20.0); HRMS calcd for $C_{15}H_{12}$ 192.0939, obsd 192.0920.

FVP of **1d** resulted in the formation of the following products.

1-Methyl-1,2-dihydrocyclopentafluorene (9d): ^{1}H NMR (CDCl$_3$) δ 1.53 and 1.56 (d, J = 7.2 Hz, 3H), 1.96−2.12 (m, 1H), 2.93−3.27 (m, 1H), 3.60−3.83 (m, 2H), 6.76−7.59 (m, 7H); MS *m/e* (relative intensity) 206 (M$^+$, 92.5), 191 (98.4), 165 (100), 89 (24.6), 76 (16.2).

2-Methyl-1,2-dihydrocyclopentafluorene (9′d). *endo*- Isomer: ^{1}H NMR (CDCl$_3$) δ 0.33 (d, J = 7.3 Hz, 3H), 2.55 (d, J = 14.2 Hz, 1H), 3.07−3.32 (m, 1H), 3.60−3.72 (m, 1H), 4.23 (d, J = 7.3 Hz, 1H), 6.87−7.62 (m, 7H); MS *m/e* (relative intensity) 206 (M$^+$, 100), 191 (92.0), 165 (88.0), 89 (31.4), 76 (26.1). *exo*-Isomer: ^{1}H NMR (CDCl$_3$) δ 1.56 (d, J = 7.2 Hz, 3H), 2.30−2.36 (m, 1H), 3.00 (dd, J = 15.2, 7.2 Hz, 1H), 3.28 (dd, J = 7.2, 5.1 Hz, 1H), 3.85 (d, J = 10.0 Hz, 1H), 7.00−7.79 (m, 7H); MS *m/e* (relative intensity) 206 (M$^+$, 90.3), 191 (99.2), 165 (100), 89 (21.7), 76 (18.9).

1-(1-Propenyl)fluorene (10d): ^{1}H NMR (CDCl$_3$) δ 3.52 (d, J = 6.0 Hz, 2H), 3.84 (s, 2H), 5.10 (dd, J = 10.0, 3.2 Hz, 2H), 5.94−6.09 (m, 1H), 7.13−7.79 (m, 7H); MS *m/e* (relative intensity) 206 (M$^+$, 28.3), 165 (100), 89 (18.1), 76 (17.7); HRMS calcd for $C_{16}H_{14}$ 206.1095, obsd 206.1089.

FVP of **1e** produced the following products.

1,1-Dimethyl-1,2-dihydrocyclopentafluorene (9e): ^{1}H NMR (CDCl$_4$) δ 1.28 (s, 3H), 1.58 (s, 3H), 1.75 (d, J = 11.2 Hz, 1H), 2.46 (dd, J = 11.2, 7.2 Hz, 1H), 4.28 (dd, J = 11.2, 7.2 Hz, 1H), 6.72−7.58 (m, 7H); MS *m/e* (relative intensity) 220 (M$^+$, 62.4), 205 (100), 165 (41.4); calcd for $C_{17}H_{16}$ 220.1252, obsd 220.1247.

2,2-Dimethyl-1,2-dihydrocyclopentafluorene (9′e): ^{1}H NMR (CDCl$_3$) δ 0.35 (s, 3H), 1.61 (s, 3H), 2.57 (d, J = 15.2 Hz, 1H), 3.49 (d, J = 15.2 Hz, 1H), 3.94 (s, 1H), 6.81−7.61 (m, 7H); MS *m/e* (relative intensity) 220 (M$^+$, 88.4), 205 (76.4), 165 (100).

1-(2-Methyl-1-propenyl)-1,2-dihydrocyclopentafluorene (10e): ^{1}H NMR (CDCl$_3$) δ 1.71 (s, 3H), 3.40 (s, 2H), 3.75 (s, 2H), 4.72 (d, J = 10.1 Hz, 2H), 6.91−7.69 (m, 7H); MS *m/e* (relative intensity) 220 (M$^+$, 37.3), 205 (26.1), 165 (100); HRMS calcd for $C_{17}H_{16}$ 220.1252, obsd 220.1245.

Preparation of 1-(1-Deuterioethyl)-9-diazofluorene (1c-*d*): A solution of 1-ethyl-9-fluorenone (500 mg, 2.4 mmol) in CCl$_4$ (10 mL) was heated to 70−75 °C and irradiated with 500 W tungsten lamp while a solution of bromine (0.42 g, 2.64 mmol) in CCl$_4$ (1 mL) was added dropwise. Evaporation of the solvent left 1-(1-bromoethyl)-9-fluorenone as a brownish oil in quantitative yield: ^{1}H NMR (CCl$_4$) δ 1.96 (d, J = 8.1 Hz, 3H), 6.44 (q, J = 8.1 Hz, 1H), 6.88−7.82 (m, 7H). The bromide (200 mg, 0.69 mmol) was added to a solution of NaBD$_4$ (52 mg, 1.38 mmol) in DMSO (4 mL); the mixture was stirred for 2 h at room temperature and then poured onto ice−water. The mixture was extracted with Et$_2$O, and the ethereal layer was dried and evaporated to leave 1-(1-deuterioethyl)-9-deuterio-9-fluorenol-*O*-*d* as a yellow oil in 90% yield: ^{1}H NMR (CCl$_4$) δ 1.08−1.36 (m, 3H), 2.76−3.08 (m, 1H), 6.71−7.70 (m, 7H); MS *m/e* (relative intensity) 212 (M$^+$, 15), 198 (72), 182 (100), 166 (29). To a stirred solution of the fluorenol (30 mg, 0.24 mmol) in acetone (1 mL) was added a solution of CrO$_3$ (42.7 mg) in diluted H$_2$SO$_4$ (0.3 mL), and the mixture was stirred for 30 min. The reaction mixture was quenched by 2-propanol and extracted with Et$_2$O. Evaporation of the solvent left 1-(1-deuterioethyl)-9-fluorenone as a yellow oil in 67% yield: ^{1}H NMR (CCl$_4$) 1.12−1.36 (m, 3H), 2.60−2.96 (m, 1H) 6.71−7.70 (m, 7H); MS *m/e* (relative intensity) 209 (M$^+$, 100), 193 (20), 180 (45). The fluorenone (180 mg, 0.56 mmol) was then converted to the corresponding diazomethane (**1c**-*d*) by using essentially the same procedure as described for **1c**: red solid; mp 74 °C; ^{1}H NMR (CDCl$_3$) δ 1.28−1.30 (m, 3H), 2.80−2.89 (m, 1H), 7.12−7.92 (m, 7H); IR (KBr) 2060 cm^{-1}. The deuterium content was calculated as 95% on the basis of ^{1}H NMR.

FVP of **1c**-*d* gave a mixture of **9c**-*d* and **9′**-*d* in 65% yield. The product ratio was estimated by integrating the protons at C$_1$ and C$_2$ and calibrating using the C$_{2a}$ proton signals. Note that all key signals were fairly well-resolved, thus making this estimate accurate.

Matrix-Isolation Spectroscopy. Matrix experiments were performed by standard techniques[46] using an Iwatani Cryo Mini closed cycle helium cryostat. For IR experiments, a CsI target was attached to the copper holder at the bottom of the cold head. Two opposing ports of the vacuum shroud were fitted with KBr windows for spectroscopic viewing, and the remaining ports were fitted with a quartz plate for UV irradiation and a deposition devise for admitting the sample and matrix gas. For the UV experiments, a sapphire cold target and quartz outer window were used. The temperature of the matrix was controlled by an Iwatani TCU-1 temperature controller.

Argon (Seitetsu Chemicals, 99.999%), oxygen (Seitetsu Chemicals, 99.9995%), and very volatile organic compounds were mixed in a gas handling system by standard manometric techniques.

Irradiations were carried out using a Wacom 500 W xenon high-pressure arc lamp or an Ushio 500 W mercury high-pressure arc lamp. For broad-band irradiation, Toshiba cut-off filters were used (50% transmittance at the wavelengths specified).

Laser Flash Photolysis. All flash photolysis measurements were made on a Unisoku TSP-601 flash spectrometer. The excitation source for the laser flash photolyses was a Quanta-Ray GCR-11 Nd:YAG laser which produced 4−5 ns fwhm pulses of up to 30 mJ at 266 nm. The beam shape and size were controlled by a focal length cylindrical lens.

A Hamamatsu 150 W xenon short arc lamp (L2195) was used as the probe source, and the monitoring beam guided using an optical fiber scope was arranged in an orientation perpendicular to the excitation source. The probe beam was monitored with a Hamamatsu R2949 photomultiplier tube through a Hamamatsu S3701−512Q MOS linear image sensor (512 photodiodes used). Timing of the laser excitation pulse, the probe beam, and the detection system was achieved through an Iwatsu Model DS-8631 digital synchroscope which was interfaced to a NEC 9801 RX2 computer. This allowed for rapid processing and storage of the data and provided printed graphics capabilities. Each trace was also displayed on a NEC CRT N5913U monitor.

A sample was placed in a long-necked Pyrex tube which had a side arm connected to a quartz fluorescence cuvette and degassed using a minimum of four freeze−degas−thaw cycles at pressures near 10^{-5} Torr immediately prior to being flashed. The sample system was sealed, and the solution was transferred to the quartz cuvette which was placed in the sample chamber of the flash spectrometer. The concentration of the sample was adjusted so that it absorbed a significant portion of the laser light. For kinetic measurements, a suitable range of concentration of trapping reagents was used, and the rate constants for the decay of the transients were determined by plotting the observed rate constant of the formation of the transient against [trapping reagents]. The plot is linear in the concentration range indicated in the text.

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