purposes in the condensed phase has yet to be demonstrated.

With the exception of $Ph_2C{=}N_2^{\bullet-}$, few data are available concerning the reactions of $R_2C{=}N_2^{\bullet-}$ with proton donors. $(EtO_2C)_2C{=}N_2^{\bullet-}$ is not protonated by relatively strong acids such as PhCOOH ($pK_a^{Me_2SO}$ = 11.0)[7] and $(CF_3)_2CHOH$.[18] Interestingly, diazodimedone anion radical[22] reacts rapidly with CF_3CH_2OH ($pK_a^{Me_2SO}$ = 23)[8] but not with $(EtO_2C)_2CH_2$ ($pK_a^{Me_2SO}$ = 16.4).[7] This difference in behavior is under current investigation.

Only two diazoalkanes that do not contain one or more carbonyl groups have been studied extensively. In the case of both 1 and diazofluorene, electroreduction initiates a chain reaction that ultimately affords the corresponding azine as the principal product. However, whereas diazofluorene anion radicals dimerize to give a tetrazine that slowly loses N_2,[23,24] $1^{\bullet-}$ is believed to react initially by hydrogen atom abstraction. As Bethell and Parker[5] have noted, hydrogen atom abstraction is an unusual reaction pathway for anion radicals. Whether or not other diazoalkanes will react by hydrogen atom abstraction or dimerization remains to be determined.

Experimental Section

Instrumentation, Cell, Electrodes, and General Procedures. The electrochemical and data acquisition equipment have been described previously.[13] All electrochemical experiments were performed on an all-glass vacuum line. Planar platinum and vitreous carbon working electrodes were used for most cyclic voltammetric and chronoamperometric experiments. All potentials listed were measured with respect to a cadmium chloride/cadmium amalgam reference electrode; the solvent in this electrode was DMF and was saturated with respect to both sodium chloride and cadmium chloride (Type A-III).[25] The potential of this electrode is −0.75 V vs. SCE. Dual reference electrodes were used in all cyclic voltammetric and chronoamperometric experiments.[26] The second reference electrode was a platinum wire which is in series with a 0.1-μF capacitor and was placed in parallel with the cadmium chloride/cadmium amalgam reference electrode.

Coulometry. The progress of large-scale electrolyses was monitored periodically by cyclic voltammetry. At the conclusion of an electrolysis, the mixture was protonated in a dry helium atmosphere with $(EtO_2C)_2CH_2$ and then analyzed by HPLC. In order to determine if the acid that was used for protonation of the anionic electrolysis products might catalyze the decomposition of unreacted 1, a tenfold excess of PhCOOH, CH_3COOH, $(EtO_2C)_2CH_2$, CF_3CH_2OH, or $(CF_3)_2CHOH$ was added to a solution of 1 in DMF.[27] With the exceptions of PhCOOH and CH_3COOH, none of the proton donors caused any discernible change in the absorption spectrum of 1 after reaction for 48 at room temperature.

Chemicals. DMF (Burdick and Jackson) was purified by passage through a column of alumina (500 g, 80–200 mesh, Brockman activity 1, activated at 600 °C overnight) and was collected over a mixture of Davison 4-Å molecular sieves and alumina. This procedure was carried out in a dry, nitrogen-filled glovebag. After purification, the solvent was transferred immediately to the vacuum line. Either $(CH_3)_4NBF_4$ or $(CH_3)_4NPF_6$ was used as the supporting electrolyte; these materials were stored in a vacuum oven over phosphorus pentoxide. $Ph_2C{=}N_2$[28] and $Ph_2C{=}NN{=}CPh_2$[29] were synthesized according to reported procedures. All other compounds were commercially available. The purities of all compounds were checked by melting point, HPLC, and/or cyclic voltammetry.

Acknowledgment. Financial support of this work by the National Science foundation is gratefully acknowledged.

Registry No. 1, 883-40-9; $1^{\bullet-}$, 75558-05-3; p-$NCC_6H_4NH_2$, 873-74-5; $Ph_2C{=}NN{=}CPh_2$, 983-79-9; $Ph_2CHN^-N{=}CPh_2$, 81667-74-5.

Supplementary Material Available: Kinetics studies of 1^{2-}, the chronoamperometric study of $1^{\bullet-}$, the plot of $n_{apparent}$ vs. log tc for 1 (Figure 3), cyclic voltammograms for the reduction of 1 (Figure 4 and 6), and the double-potential-step chronoamperometric data for the reduction of 1 (Figure 5) [see text for specific conditions] (7 pages). Ordering information is given on any current masthead page.

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An Investigation of 1,8-Diazafluorenylidene. A Carbene with Unusual Properties

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Received January 14, 1986

Irradiation of 9-diazo-1,8-diazafluorene initiates a series of photochemical reactions that lead to isomerization to the diazirine and to loss of nitrogen to form a carbene. The carbene has a triplet ground state but reacts primarily from its upper singlet state. The chemical and physical properties of the diazo compound and the carbene are compared with those for 9-diazofluorene. The differences between these compounds are assigned tentatively to a combination of through-space interaction of the lone pair electrons of the heteroatomic ring atoms with the nonbonding in-plane orbital of the carbene carbon and the electron-withdrawing nature of the pyridine-like nitrogens.

The chemical and physical properties of carbenes vary widely in response to the electronic character of the attached substituent groups.[1] This has long been recognized for simple methylenes and an empirical correlation has been developed that relates the properties of the substituents to the properties of the carbenes.[2] The issue is considerably more complex in the case of diarylcarbenes.

Arnold and co-workers, in a seminal study, attempted to invert the normal ordering of triplet diphenylcarbene

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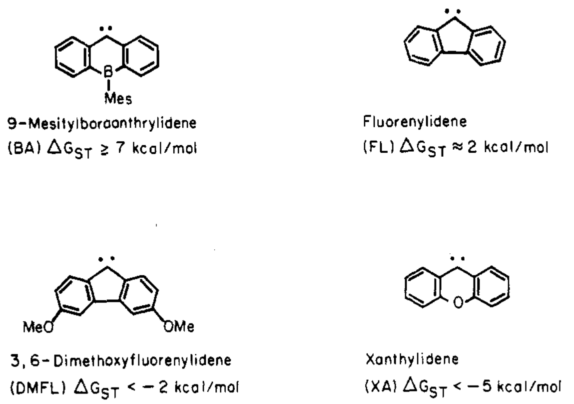
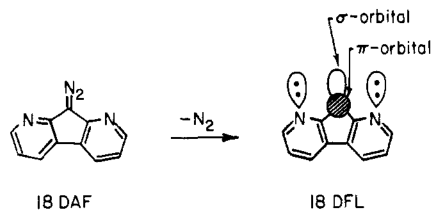
Scheme I



Scheme II



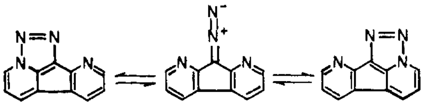
below the singlet by choosing substituents thought to be specially suited for stabilizing the singlet state through resonance.[3] This attempt failed. EPR spectroscopy revealed a triplet ground state for all the substituted diphenylcarbenes examined. However, these substituents could certainly be affecting the gap (ΔG_{st}) between the states without inverting their order.

A more satisfying result was obtained from examination of the "derivatives" of fluorenylidene (FL) shown in Scheme I.[4-8] Our investigations of these carbenes revealed that ΔG_{st} is a smooth function of the electronic properties of the carbene. The ground states of BA and FL are triplets, while DMFL and XA have singlet ground states. The effect of the "substituents" on these carbenes is easily understood from the simplest application of perturbation molecular orbital theory.[9] In this approach the substituent effect is transmitted through the π-system of the arene to the p-type orbital of the carbene. Raising or lowering the energy of this orbital with respect to the nearly stationary σ-type carbene orbital readily accounts for the observed fluctuation in ΔG_{st}.

It is a more difficult matter to manipulate specifically the relative energy of the σ-orbital of an arylcarbene. This orbital is in the nodal plane of the presumably planar carbene π-systems illustrated in Scheme I. Thus, this orbital should not respond dramatically to substituents that affect primarily the π-electrons.[10] In consideration of this problem, we undertook the examination of 1,8-diazafluorenylidene (18DFL). This carbene can be generated from 9-diazo-1,8-diazafluorene (18DAF), Scheme II. Our investigation reveals that the properties of both 18DAF and 18DFL are remarkably different from those of their parents 9-diazofluorene (DAF) and FL.

Results

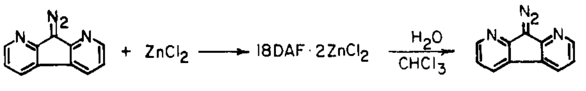
1. Preparation and Characterization of 18DAF. The preparation of 18DAF by oxidation of the appropriate hydrazone was reported by Schönberg and Junghans in 1962.[11] The properties of the material we obtain from a similar procedure are identical with those previously reported. However, the chemical behavior of 18DAF is so unlike that of other aryl diazo compounds we have studied that further characterization of this substance was needed. In particular, we considered the possibility that 18DAF may exist as a rapidly equilibrating mixture of its cyclized valence tautomeric forms as shown in eq 1.[12] If tautomerization is rapid, the C_2 symmetry revealed by ^{1}H NMR spectroscopy could be maintained even though the diazo compound is not present. This possibility was eliminated by comparing the strength of the characteristic infrared absorption band of 18DAF at 2100 cm^{-1} with that of diazofluorene. These two compounds exhibit diazo bands of nearly the same intensity. This observation halts further consideration of the valence tautomers shown in eq 1 and



(1)

similarly precludes assignment of the structure of this substance to the diazirane. However, diazirine formation does play an important role in the photochemistry of 18DAF (see below).

2. Acid-Catalyzed and Thermal Reactions of 18DAF. The Lewis acid initiated reaction of diazo compounds with olefins is an efficient way to prepare cyclopropanes.[13] Indeed, DAF reacts with styrene nearly instantaneously at −10 °C when $ZnCl_2$ is used as a catalyst. In contrast, addition of $ZnCl_2$ to a solution of 18DAF and styrene at 30 °C does not generate any cyclopropane. This reaction yields a precipitate shown by quantitative elemental analysis to be a complex of 18DAF and $ZnCl_2$. The diazo compound can be recovered unchanged from this complex by simple hydrolysis, eq 2. Similarly, addition of 10% $HClO_4$ to a methyl alcohol solution of 18DAF at 80 °C does not lead to denitrogenation. DAF loses nitrogen rapidly under these conditions.



(2)

Thermolysis of diazo compounds usually causes smooth nitrogen loss at relatively low temperature. For example, DAF has a half-life of about 30 min in diphenyl ether at 140 °C. Under these conditions, 18DAF has a half-life of at least 2 days. It is clear that loss of a nitrogen from 18DAF is a much less facile process under a variety of conditions than it is for DAF.

3. Photolysis of 18DAF in Frozen Media. The most certain way to detect a triplet carbene is to observe its EPR spectrum.[14] Irradiation of 18DAF in Fluorolube at 77 K gives a paramagnetic intermediate readily characterized

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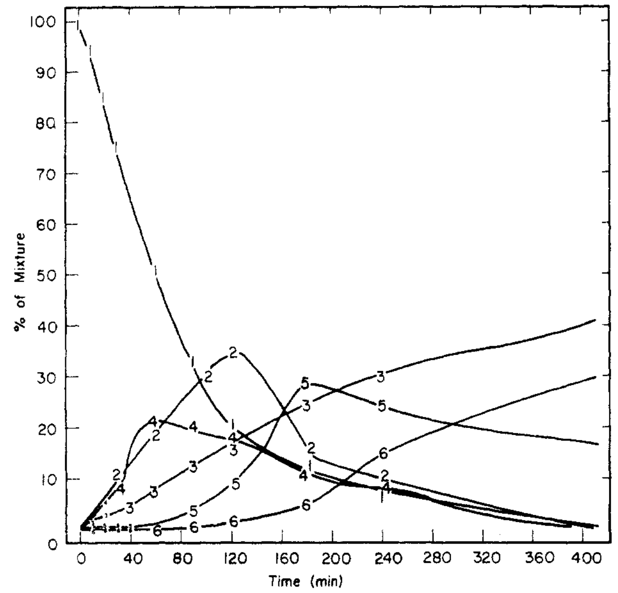
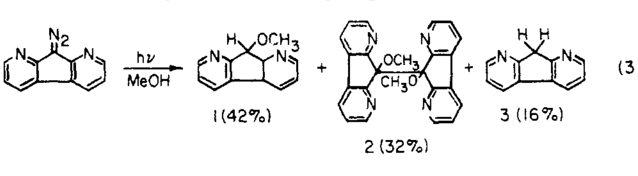


Figure 1. Irradiation of 18DAF in methyl alcohol. The numbers on the plots correspond to data points obtained from integration of the ^{1}H NMR spectra. They correspond to 1 = 18DAF, 2 = diazirine 4, 3 = dimeric ether 2, 4 = unknown product with chemical shift δ 3.70, 5 = ether 1; 6 = diazafluorene 3.

as ^{3}18DFL. The EPR signals characteristic of the carbene are stable for at least several hours in this medium at the low temperature. Fitting the observed spectrum to the usual spin Hamiltonian[15] gives the zero-field parameters $|D| = 0.442$ cm^{-1} and $|E| = 0.029$ cm^{-1}. These values are quite similar to those obtained from a related experiment on DAF.[16] These results show that the ground state of 18DFL is a triplet and that the structure of this triplet is very similar to that of ^{3}FL.

The EPR spectrum of ^{3}18DFL can be observed in 2-methyltetrahydrofuran (MTHF) at ca. 4 K. However, if this sample is warmed to 77 K the signal disappears. Similarly, irradiation of 18DAF in MTHF at 77 K does not give an observable EPR signal. These observations are consistent with an extraordinarily high degree of reactivity for 18DFL.

4. Photolysis of 18DAF in Methyl Alcohol. Irradiation of diazo compounds in solution typically leads to efficient generation of a carbene that undergoes characteristic chemical changes. Photolysis of 18DAF in methyl alcohol (350 nm) initiates a complex series of reactions that lead eventually to three major products, eq 3. These



1 (42%) 2 (32%) 3 (16%) (3)

products were isolated by chromatography and their structures determined by conventional means as described in the Experimental Section.

The time course of the photolysis of 18DAF in methyl alcohol is readily determined by examination of the proton NMR spectrum of the reaction mixture. The results of this experiment are illustrated in Figure 1. We were surprised to discover that methyl 1,8-diazafluorenyl ether (1) is not a primary product of the reaction. Formation of this ether begins only after an induction period of ca. 60 min under these photolysis conditions. This behavior indicates that ether 1 is formed as a consequence of the subsequent reaction of some initial photoproduct.

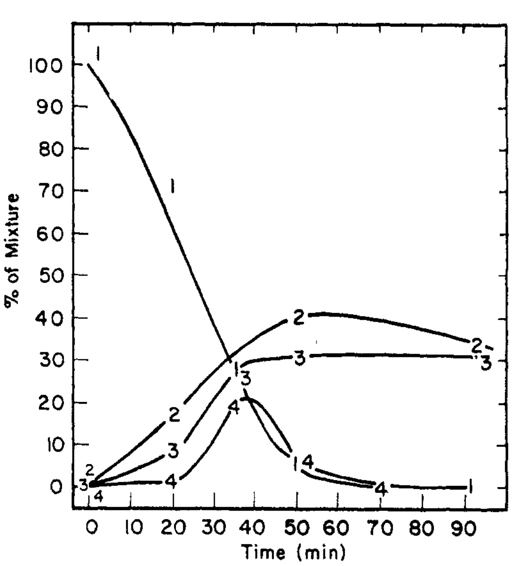
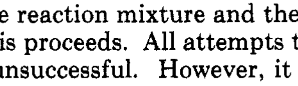


Figure 2. Irradiation of diazirine 4 in methyl alcohol. The numbers on the plot correspond to data points obtained from analysis of ^{1}H NMR spectra. They correspond to 1 = diazirine 4, 2 = ether 1, 3 = dimeric ether 2, 4 = unknown product with chemical shift at δ 3.70.

One of the initial photoproducts formed from irradiation of 18DAF can be isolated by chromatography of reactions carried only to partial conversion (2-h irradiation, Figure 1). This product is an isomer of the diazo compound and reverts in part to 18DAF on thermolysis or photolysis. Its IR spectrum does not show a diazo absorption band and its ^{1}H NMR spectrum exhibits three groups of resonances characteristic of a 1,8-diazofluorenyl ring that is symmetrically substituted at the 9-position. On the basis of this evidence, and other findings (vide infra), we assign the structure of this primary photoproduct to the 1,2-diazirane 4 shown in eq 4. Photoisomerization of diazo ketones to

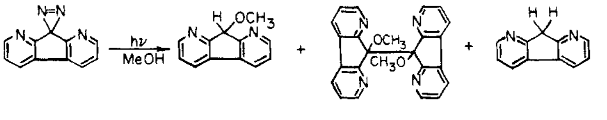


4 (4)

diazirines has been observed previously.[1] But, to the best of our knowledge, this is the first example of this rearrangement for a diaryl diazo compound.

Formation of diazirine 4 accounts for only part of the complexity evident from inspection of Figure 1. In particular, at short reaction times an unstable product, characterized by a methoxy resonance at δ 3.70, is seen to grow into the reaction mixture and then to disappear as the photolysis proceeds. All attempts to isolate this material were unsuccessful. However, it is apparent from Figure 1 that this substance is a primary product of photolysis of 18DAF. This is especially clear from consideration of Figure 2.

Photolysis of diazirine 4 leads ultimately to the same products as are obtained from irradiation of 18DAF, eq 5. However, the order in which the products appear is



(5)

not identical with that from 18DAF. In particular, ether 1 is a primary product of irradiation of the diazirine, and the unknown material with the proton resonance of δ 3.70 is a secondary product in this case.

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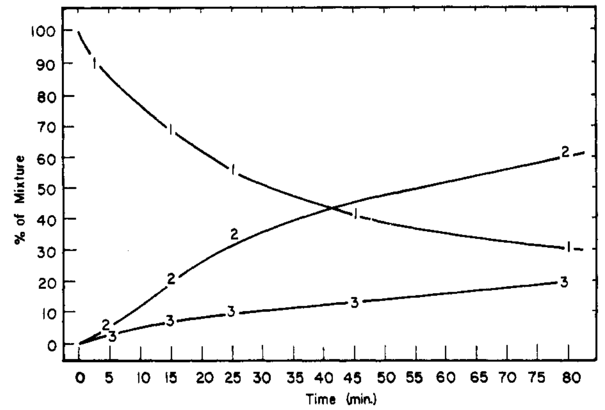
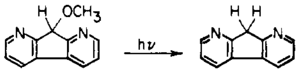


Figure 3. Irradiation of 18DAF in cyclohexane. The numbers correspond to data points obtained by integration of the ^1H NMR spectra. They correspond to 1 = 18DAF, 2 = cyclohexyldiazafluorene **5**, 3 = diazirine **4**.

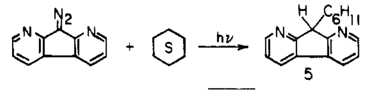
These observations allow us to infer that formation of ether **1**, presumably a product characteristic of the generation of the carbene,[17] occurs efficiently from irradiation of the diazirine and inefficiently from photolysis of the diazo compound. Similarly, the unstable methyl alcohol incorporation product comes uniquely from photolysis of 18DAF. We suspect that this material is formed by addition of the alcohol to the excited diazo compound. Also, we are able to show independently that the 1,8-diazofluorene (**3**) isolated from these reactions is formed from secondary photolysis[6,18] of ether **1**, eq 6. Finally, the



(6)

findings indicate that dimeric diether **2** is formed from photolysis of the unstable "3.70" product. However, this suggestion is tentative since the structure of the unisolated compound is unknown.

5. Direct Photolysis of 18DAF in Cyclohexane. Irradiation of 18DAF in cyclohexane leads cleanly to 9-cyclohexyl-1,8-diazafluorene (**5**) in 95% yield, eq 7. Examination of this reaction at partial conversion reveals the evanescent formation of diazirine **4**, Figure 3.

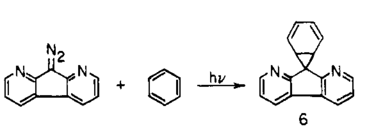


(7)

Formation of insertion product **5** is indicative of the intermediacy of the carbene 18DFL. The spin multiplicity of the carbene that gives rise to **5** was probed by using isotope tracer and product isotope effect techniques. If **5** arises from the abstraction–recombination route characteristic of triplet carbenes,[1] then irradiation of 18DAF in a 1:1 mixture of C_6H_{12} and C_6D_{12} should lead to crossover in **5**. On the other hand, if **5** is formed by the direct insertion path characteristic of singlet carbenes,[19] then irradiation in the isotopically mixed solvent should give only h_{12} and d_{12} products. Analysis by FI mass spectrometry of the product formed in this experiment shows that crossover accounts for less than 3% of the reaction. This indicates operation of the direct insertion route characteristic of a singlet carbene.

An identical mechanism is inferred from analysis of the product isotope effects. It is generally observed that the isotope effect for abstraction of hydrogen by a triplet carbene is ca. 4–8 while insertion into a carbon–hydrogen bond by a singlet carbene proceeds with an isotope effect of only ca. 1–2.[5,6,20] Analysis of the products formed from irradiation of 18DAF in the mixture of C_6H_{12} and C_6D_{12} reveals an isotope effect on product formation of 1.2 ± 0.1.

6. Direct Photolysis of 18DAF in Benzene. Irradiation of 18DAF in benzene leads to inpermanent generation of diazirine **4** and finally to the norcaradiene product **6**, eq 8. Addition of a carbene to benzene is a

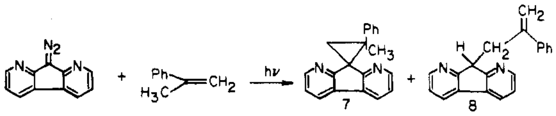


(8)

process characteristic of an electrophilic singlet state.[21] Norcaradiene **6** can be isolated in ca. 75% yield. It is unstable to further irradiation which converts it to a dimeric material.

7. Direct Photolysis of 18DAF in Benzene Containing α-Methylstyrene. The most characteristic reaction of a carbene is its addition to an olefin to form a cyclopropane. We examined the reaction of 18DFL with α-methylstyrene under a range of conditions.

Irradiation of 18DAF in benzene containing 1.0 M α-methylstyrene does give the expected cyclopropane (**7**), but its yield is only ca. 10%. The major product of this reaction is the norcaradiene **6** formed by addition of the carbene to the solvent. This finding is remarkable when compared with the photolysis of DAF which gives the appropriate cyclopropane in nearly quantitative yield under these conditions.[4] Not surprisingly, increasing the concentration of the styrene in benzene leads to a higher yield of cyclopropane from irradiation of 18DAF. In neat α-methylstyrene, the cyclopropane is formed in 87% yield and a second product (**8**) arising from insertion of the carbene into a carbon–hydrogen bond of the methyl group is formed in 13% yield, eq 9.



(9)

The stereochemistry of cyclopropane formation is classically used as an indicator of the spin multiplicity of the reacting carbene.[22] We employed specifically deuterated α-methylstyrene to probe this aspect of 18DAF. Irradiation of 18DAF in neat (*E*)-β-deuterio-α-methylstyrene gives the cyclopropane **7** with 95 ± 10% retention of configuration. This observation is consistent with the notion that the formation of cyclopropane **7** under these conditions originates exclusively from reaction of the singlet carbene.

8. Triplet-Sensitized Reactions of 18DAF. Triplet-sensitized photoreactions of diazo compounds are commonly used to bypass the singlet-state intermediates and to give directly a triplet carbene. In this way, under favorable circumstances, the chemistry of the singlet carbene can be separated from that of the triplet.

The phosphorescence of triplet benzil is quenched rapidly by 18DAF. This reaction leads to consumption of the diazo compound and to the appearance of characteristic carbene products. This sensitized irradiation of 18DAF is inhibited by low concentrations of anthracene—an observation which confirms the operation of a triplet energy transfer mechanism, Tables I and II.[23]

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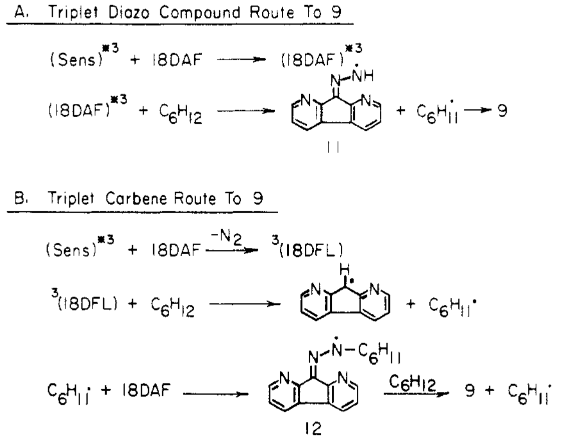
Table I. Benzil-Sensitized Photolysis of 18DAF in Benzene Containing α-Methylstyrene[a]

			product yields (%)[b]		
expt	sensitizer	quencher	18DAF	6	7
A	none	none	82	10	3
B	benzil[c]	none	5	4	85
C	benzil	anthracene[d]	90	3	6

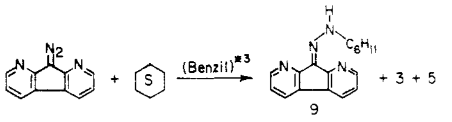
[a] All samples contained 5.2×10^{-3} M 18DAF and 0.95 M α-methylstyrene. They were irradiated simultaneously through a Corning cutoff filter. [b] Absolute yields. [c] Benzil concentration is 5.9×10^{-2} M. [d] Anthracene concentration is 3×10^{-2} M.

Scheme III



Triplet benzil sensitized reactions of 18DAF in benzene containing α-methylstyrene are specially informative (Table I). Note in particular that under conditions where the direct irradiation of 18DAF gives only a 10% yield of cyclopropane **7**, the sensitized reaction gives a nearly quantitative yield (based on 18DAF consumed). The small amount of norcaradiene product formed in these reactions is due to light unavoidably absorbed directly by the diazo compound. Further, we find that benzil-sensitized reactions of 18DAF with the deuterated methylstyrene gives the cyclopropane with complete loss of stereochemistry. These results show clearly that sensitization does generate 18DFL, that this carbene has a triplet ground state, and that it behaves much like many other triplet carbenes.

The triplet-sensitized photolysis of 18DAF in cyclohexane initiates a new process. The major product (60%) isolated from this reaction is the hydrazone **9** formed by the formal addition of cyclohexane to the diazo compound, eq 10. The structure of **9** was confirmed by independent synthesis. Lesser amounts of diazafluorene **3** and adduct **5** also result from triplet sensitization of 18DAF in cyclohexane.



(10)

In principle, hydrazone **9** could arise from at least two distinct routes. The first starts with reaction of the triplet diazo compound with cyclohexane and gives **9** in one or several steps. The second features hydrogen abstraction by the triplet carbene to generate the cyclohexyl radical which in turn reacts with 18DAF to give **9**. These paths are summarized in Scheme III. We performed a series of experiments to distinguish between these possibilities.

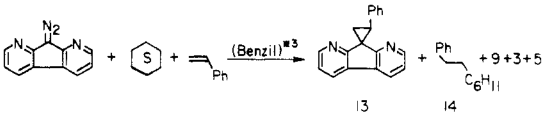
Table II. Benzil-Sensitized Photolysis of 18DAF in Cyclohexane Containing Styrene[a]

		product yields (%)[b]		
[styrene], M[c]	13	9	5	3
0		60	15	29
0.08	11	45	14	37
0.17	26	29	10	28
0.32	58	8	7	13
0.51	81	ND[d]	8	6
1.06	91	ND	6	5

[a] Concentration of 18DAF = 5.2×10^{-3} M, benzil = 4.8×10^{-2} M. All solutions were purged with N_2 before irradiation with light of wavelength greater than 380 nm. [b] Absolute yields determined by gas chromotography. [c] If anthracene, 1.0×10^{-2} M, is included in the reaction mixture >80% of the diazo compound is recovered unreacted. [d] None detected.

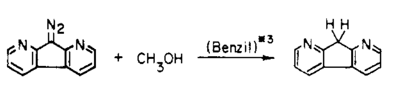
If the triplet diazo compound is the precursor to **9**, as in Scheme IIIA, then a low concentration of styrene should not interfere with the formation of radical **11**. Alternatively, if the carbene is the precursor to **9**, then cyclopropanation of styrene should compete with hydrazone formation.

Benzil-sensitized reactions of 18DAF in cyclohexane containing small amounts of styrene gives two new products, the expected cyclopropane **13** and (2-cyclohexylethyl)benzene (**14**), eq 11. The formation of **14** confirms the presence of cyclohexyl radical in the reaction mixture. The dependence of the product composition on the concentration of styrene is summarized in Table II. The yield of hydrazone **9** decreases as the styrene concentration increases, and, simultaneously the formation of cyclopropane **13** becomes more significant. This finding is consistent only with mechanisms where cyclopropane formation competes with hdyrazone production as is the case in Scheme IIIB. Also, we showed independently that cyclohexyl radical in cyclohexane does react with 18DAF to give **9**.



(11)

Finally, we explored the benzil-sensitized reaction of 18DAF in methyl alcohol. In contrast to the complex behavior observed for the direct irradiation, triplet sensitization gives only one product, diazafluorene **3**, isolated in 79% yield, eq 12. This result is particularly meaningful in comparison with the direct and triplet-sensitized reactions of DAF with methyl alcohol which both give high yields of the ether.



(12)

Discussion

The properties of 18DAF and 18DFL are remarkably different from those of their conceptual parents DAF and FL. The heterocyclic diazo compound exhibits extraordinary stability at high temperature or in the face of Lewis or protic acids, and its irradiation causes tautomerization to the diazirine in competition with nitrogen loss. The chemical properties of the heterocyclic carbene, in contrast to those of FL, depend strongly on the way in which it is generated and on details of the chemical environment. These results must be understood by consideration of the perturbation caused by substitution of the nitrogen atoms into the parent fluorenylidene structure.

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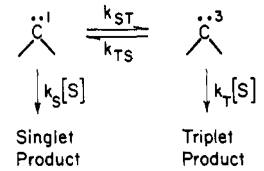
(23) The triplet energy of benzil is 54 kcal/mol, that of anthracene is 43 kcal/mol. Thus, the energy of triplet of 18DAF must be between these two values.

Scheme IV



The chemical properties of carbenes, such as those identified in Scheme I, are readily organized by a model in which the singlet and triplet states are close in energy, and, under some circumstances, equilibrate faster than they undergo irreversible bimolecular reaction.[1] This interpretation is illustrated in Scheme IV. With this scheme it is easy to explain the quite different properties displayed by these carbenes by analyzing the effect of structural perturbation on the magnitude of the equilibrium constant connecting the carbene spin states ($K_{eq} = k_{st}/k_{ts}$) and the rate constants k_t and k_s.

The effect of structural variation on carbene properties has generally been separated into steric, primarily the carbene carbon bond angle,[24] and electronic components. It is reasonable to expect that the carbene–carbon bond angle is the same for both 18DFL and FL since both compounds have similar structural frameworks. This supposition is confirmed by the nearly identical zero-field parameters displayed by the triplets. Thus, we must explain the different properties of 18DFL and FL solely on the basis of the electronic perturbation associated with the placement of the nitrogen atoms at positions 1 and 8 of the fluorene nucleus.

The EPR spectroscopic results demonstrate convincingly that the ground state of 18DFL is a triplet. The chemical properties of the triplet are clearly revealed in the sensitization experiments. Its reactions with α-methylstyrene, cyclohexane, and methanol are indicative of a radical-like species prone to hydrogen atom abstraction and radical pair formation. Similar behavior is observed for many ground-state triplet carbenes and in this regard 18DFL is unexceptional.

The direct irradiation of 18DAF leads eventually to products indicative of the generation of the carbene. The intermediate formation of diazirine 4 and the complex behavior in methyl alcohol obscure the behavior of this compound. But, the direct irradiation in cyclohexane, benzene, and α-methylstyrene are easily interpreted. In each of these three cases, the reaction the carbene exhibits are those characteristic of the singlet state. This occurs despite the firm conclusion that 18DFL has a triplet ground state. These findings are consistent with the model displayed in Scheme IV. They simply indicate that the rate of the irreversible bimolecular reaction of the singlet carbene (k_s[S]) is faster than its intersystem crossing to the ground-state triplet (k_{st}). Also, the rate of reaction of the triplet carbene (k_t[S]) must be greater than its conversion to (k_{ts}) and reaction from the singlet state.

Unfortunately, all attempts to observe 18DFL spectroscopically on a picosecond or a nanosecond timescale by photolysis of either 18DAF or the diazirine were unsuccessful. This unhappy circumstance is a consequence of the reaction of the singlet carbene before it intersystem crosses to the triplet. Triplet carbenes can be observed spectroscopically because of their strong absorptions in the visible spectral region.[14] Singlet carbenes apparently absorb light at shorter wavelengths than the corresponding triplets.[5,6] The design of our picosecond spectrometer restricts analyzing wavelengths to those greater than ca. 430 nm. Evidently, all of the strong absorptions of ^{1}18DFL occur at wavelengths below this limit.

Nevertheless, it is possible to make a semiquantitative comparison of the reactivity of 18DFL and FL based on our observations. The rate constants for intersystem crossing (k_{st}) of several diaryl carbenes with triplet ground states have been measured.[4,5,25] These values are generally found to be approximately 10^{10} s^{-1}. Since we known that the ground state of 18DFL is the triplet, that direct irradiation of 18DAF in cyclohexane, for example, gives only products characteristic of the singlet carbene, and that sensitization gives typical triplet carbene products, we can conclude that the reaction of ^{1}18DFL with cyclohexane is so much faster than k_{st} that none (less than 5%) of the triplet is formed. Thus, the rate of reaction of the singlet (k_s[S]) must be at least 20 times greater than k_{st}. With the assumption that k_{st} is approximately the same for 18DFL as it is for those cases where this rate constant has been determined, we estimate, by application of eq 13, that

$$k_s[S] \gtrsim 20k_{st} \qquad (13)$$

k_s for cyclohexane is ca. 2×10^{10} M^{-1} s^{-1}. This value is essentially the diffusion encounter limit. And, significantly, it is several hundred times greater than the corresponding value measured for FL.[4]

A similar conclusion is reached from consideration of the results of photolysis of 18DAF in benzene containing α-methylstyrene. The ratio of cyclopropane to norcaradiene products obtained reflects approximately the mole ratio of the styrene and benzene in the reaction mixture. This is easily understood if ^{1}18DFL reacts indiscriminantly with whichever trapping reagent it encounters first, i.e., $k_s \sim 2 \times 10^{10}$ M^{-1} s^{-1}. Comparison of this estimate with the corresponding values for FL again reveals that ^{1}18DFL is the much more reactive species of the two.[4]

All of our findings are consistent with the conclusions that ^{1}18DFL is considerably more reactive than other diarylcarbene singlets and that ^{3}18DFL behaves essentially like other typical triplet carbenes. We suggest that the enhanced reactivity of ^{1}18DFL and the enhanced stability of 18DAF have, at least in part, a common conceptual origin: the interaction of the lone-pair electrons of the ring nitrogen atoms and the electron-withdrawing properties of the pyridine-like nitrogens.

The singlet state of methylene (CH_2) is best described as a hybrid composed of contributions from both σ^2 and p^2 electronic configurations. The nonbonding electrons of the ring nitrogen atoms of 18DFL are in orbitals with proper symmetry to interact with the in-plane σ-orbital of the carbene. This interaction resembles that of the three-orbital allyl system and similarly forms a bonding, nonbonding, and antibonding triad of σ-molecular orbitals. The σ^2 carbene electronic configuration places six electrons in these three orbitals and thus the antibonding orbital would be occupied. Simultaneously, the ring nitrogen atoms will stabilize the p^2 electronic configuration due to their increased electronegativity and their direct conjugation with the carbene carbon. We suggest that these two effects conspire to modify the electronic properties of ^{1}18DFL so much that the major contribution to this state is from the p^2 configuration. This leaves the carbene with a nearly vacant σ-orbital. The increased electrophilicity of ^{1}18DFL is then a direct consequence of higher reactivity of a vacant σ-orbital than that of a π-orbital. Structures

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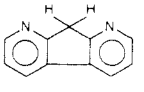
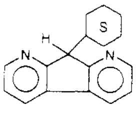
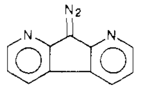
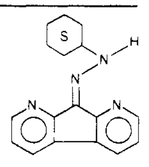
(24) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485.

(25) Sitzmann, E. V.; Eisenthal, K. B. *Applications of Picosecond Spectroscopy to Chemistry*; Reidel: New York; 1983, p 41.

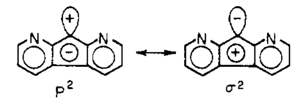
Table III. Triplet Sensitization of 18DAF in Cyclohexane

	yields (absolute), %			
sample[a]				
A	0	0	100	0
B	0	20	80	0
C	23	15	0	60
D	0	9	83	0

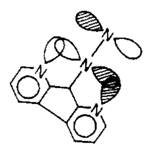
[a] See Experimental Section for details of sample composition.

Scheme V

A. Valence Bond Structures For ^{1}18DFL



B. σ − π Backbonding in 18DAF



representing these electronic configurations are drawn as resonance hybrids in Scheme VA.

The extraordinary stability of 18DAF can be accommodated by a similar rationalization. In this case, σ–π backbonding of the lone-pair electrons of the ring nitrogen, which are properly disposed for interaction with an antibonding π-orbital on the α-nitrogen of the diazo group, could increase the barrier for denitrogenation. This interaction is illustrated in Scheme VB and operates in concert with an expected increase in the 9-carbon–α-nitrogen bond order due to the increased electronegativity caused by the ring nitrogen atoms. It is tempting to speculate that the observed isomerization of 18DAF to the diazirine is a consequence of the increased bonding illustrated in Scheme V.

The relative importance of the spatial orientation of the ring-nitrogen lone-pair electrons and the increased electronegativity of the nitrogen atoms cannot be assessed for 18DFL and 18DAF with the data in hand. However, comparison of these compounds with their 3,6-diaza isomers should permit ready analysis of these forces. This system will be the subject of a forthcoming report.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a Varian EM-390 (90 MHz) or a Varian XL-200 (200 MHz, FT) spectrometer in deuteriochloroform. Mass spectra were obtained with a Varian MAT CH-5 or 731 mass spectrometer. Direct photolyses were carried out in a Rayonet photochemical reactor with 350-nm lamps and the sensitization experiments were performed by irradiation with an Oriel mercury lamp equipped with a filter that cuts off light below 380 nm.

Preparation of 9-Diazo-1,8-fluorene (18DAF). 1,8-Diazafluorenone, 1,8-diazafluoren-9-one hydrazone, and 9-diazo-1,8-diazafluorene were prepared from phanquone according to literature procedures:[11] mp for 18DAF 94.0–95.0 °C; MS (EI), *m/e* 194.0 (M$^+$), 166.0; IR (CHCl$_3$) 2091 cm^{-1} (s); NMR (CDCl$_3$) δ 7.25 (dd, J = 7.5, 3.0 Hz, 2 H), 8.12 (dd, J = 7.5, 1.5 Hz, 2 H), 8.48 (dd, J = 3.0, 1.5 Hz, 2 H).

Thermal Decomposition of 18DAF and DAF. Two samples were prepared, one contained 18DAF (20 mg) dissolved in 5 mL of diphenyl ether and the other contained DAF (18 mg) in 5 mL of diphenyl ether. The solutions were placed in tubes equipped with stopcocks and heated at 140 °C. The samples were analyzed by IR spectroscopy. The DAF was consumed completely in 3 h; 18DAF was still present after 2 d.

Reaction of 18DAF with ZnCl$_2$. ZnCl$_2$ (1.0 g) was placed in a 25-mL three-necked flask and was heated at reduced pressure (1–2 torr) until it fused. The flask was cooled in dry ice and ethyl ether (7 mL) was added followed by a solution of 18DAF. A precipitate formed immediately. The precipitate was washed three times with 10 mL of ether and then dried. Calcd for $C_{11}H_6N_4Cl_4Zn_2\cdot 1.5H_2O$: C, 26.7; H, 1.8; N, 11.3; Zn, 26.5; Cl, 28.7. Found: C, 27.9; H, 1.9; N, 11.0; Zn, 25.4; Cl, 28.6. The material is hygroscopic, and analysis of different samples indicates variable water content. The precipitate gave 18DAF almost exclusively when it was treated with water and chloroform.

Direct Photolysis of 18DAF in Cyclohexane. A 5.0 × 10^{-3} M solution of 18DAF in cyclohexane in a quartz tube was purged with argon for 15 min and then irradiated (Rayonet) until 95% of the IR absorption band of 18DAF at 2091 cm^{-1} had disappeared. The solvent was removed at room temperature, first using a rotary evaporator and then at high vacuum. The crude product was analyzed by ^{1}H NMR spectroscopy which showed only **5**. The product was purified by silica gel chromatography. Elution with benzene–ether (1:1, v/v) gave **5** in 80% yield: ^{1}H NMR (CDCl$_3$) δ 1.0–1.8 (m, 10 H), 2.55 (m, 1 H), 3.85 (d, 1 H), 7.20 (m, 2 H), 7.95 (m, 2 H), 8.55 (m, 2 H); MS (EI), *m/e* 250.0; exact MS calcd for $C_{17}H_{18}N_2$ *m/e* 250.1458, found 250.1464.

Triplet Sensitization of 18DAF in Cyclohexane. Four samples were prepared, each contained 5.1 × 10^{-3} M of 18DAF dissolved in cyclohexane (5 mL). Sample A was covered with aluminum foil to exclude light; samples C and D contained benzil (4.7 × 10^{-2} M) as a triplet sensitizer; and sample D also contained 3 × 10^{-2} M anthracene as a triplet quencher. The four samples were purged with argon, irradiated (Oriel lamp) for 1 h, and then analyzed by GC. The yields of the products was calculated with methyl stearate added as an internal standard and are reported in Table III. 1,8-Diazafluorene (**3**) and the hydrazone **9** were isolated from the reaction mixture by chromatography on a 2-mm silica gel glass-backed plate with benzene ethyl ether (1:1, v/v) as eluant. For **3**: MS, *m/e* 168.0; exact MS calcd for $C_{11}H_8N_2$ *m/e* 168.0677, found 168.0682; ^{1}H NMR for **3** (CDCl$_3$): δ 4.12 (s, 2 H), 7.30 (m, 2 H), 8.05 (m, 2 H), 8.58 (m, 2 H). For **9**: MS, *m/e* 278.0; exact MS for $C_{17}H_{18}N_4$ *m/e* 278.1351, found 278.1351. ^{1}H NMR for **9** (CDCl$_3$): δ 1.0–1.9 (m, 10 H), 2.25 (m, 1 H), 3.80 (m, 1 H), 7.20 (m, 2 H), 8.00 (m, 2 H), 8.55 (m, 2 H).

1-*N*-Cyclohexyl-1,8-diazafluoren-9-one Hydrazone. 1,8-Diaza-9-fluorenone (182 mg) was mixed with 150 mg of cyclohexylhydrazine hydrochloric acid salt (prepared according to the literature procedures[26]) and added to a mixture of 20 mL of ethanol and 10 mL of pyridine. The solution was heated at 70 °C for 2 h. The hydrazone was crystallized and found to be identical with that obtained from sensitized photolysis of 18DAF in cyclohexane.

Reaction of 18DAF in Cyclohexane and Cyclohexane-*d*$_{12}$. 18DAF (2.5 mg) was dissolved in a 1:1 mixture of cyclohexane and cyclohexane-d_{12} (total 2.1 g). The solution was purged with

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(26) Ghali, N. I.; Venton, D. L.; Hung, S. C.; Le Breton, G. C. *J. Org. Chem.* **1981**, *46*, 5413.

N_2 and irradiated for 1.5 h (95% of the 18DAF was converted into products). The mass spectrum of the insertion product **5** formed in this irradiation indicates that only 2.3% of crossover product was formed.

Sensitization of 18DAF in Cyclohexane with Styrene. Six samples were prepared; each contained 2.4×10^{-3} M 18DAF and 2.6×10^{-2} M benzil in 5 mL of cyclohexane. The samples also contained a variable amount of styrene (0–1.06 M). The solutions were purged with argon and irradiated (Oriel lamp) and then analyzed by GC with methyl stearate added as internal standard. The reaction products and their yields are reported in Table II.

Photolysis of 18DAF in Benzene. A 5×10^{-3} M solution of 18DAF in benzene was purged with Ar and irradiated (Rayonet). The ^{1}H NMR spectrum of the crude reaction mixture showed that the yield of **6** was ca. 75%. This product was isolated by chromatography on silica gel: ^{1}H NMR δ 3.95 (q, J = 2.0 Hz, 2 H), 6.15 (m, 2 H), 6.50 (q, J = 2.0 Hz, 2 H), 7.20 (dd, J = 7.5, 3.0 Hz, 2 H), 7.95 (dd, J = 7.5, 1.5 Hz, 2 H), 8.60 (dd, J = 3.0, 1.5 Hz, 2 H); exact MS for **6** calcd for $C_{17}H_{12}N_2$ m/e 244.0984, found 244.0992.

Reaction of 18DAF with α-Methylstyrene in the Presence of Benzil as a Sensitizer. A 5.15×10^{-3} M solution of 18DAF in benzene containing 1.0 M α-methylstyrene and 4.7×10^{-2} M benzil was purged with argon and irradiated (Oriel lamp) until 90% of 18DAF had disappeared (by GC analysis). Analysis of the reaction mixture by ^{1}H NMR spectroscopy showed that the yield of **6** was <5% and that of **7** was 85%. Compound **7** was isolated from the reaction mixture by chromatography on silica gel eluting with benzene–ether (1:2 v/v): ^{1}H NMR δ 2.0 (s, 3 H), 2.5 (d, 1 H), 2.8 (d, 1 H), 7.1–7.5 (m, 8 H), 8.0 (m, 2 H), 8.5 (m, 1 H); MS (EI), m/e 284.0; exact MS calcd for $C_{20}H_{16}N_2$ m/e 284.1315, found 284.1314.

A similar experiment in which the deuterated α-methylstyrene (0.47 M) was used gave **7** with total randomization of stereochemistry.

Direct Photolysis of 18DAF in Methyl Alcohol. (A) A 3.6×10^{-3} M solution of 18DAF in neat methyl alcohol was purged with argon and irradiated (Rayonet) until 95% of 18DAF was converted into products. ^{1}H NMR spectral analysis gave the yields of the three major products as 1,8-diazafluorene, 16%, the methyl ether **1**, 42%, and dimer **2**, 32%. These products were separated on silica gel eluted with an acetonitrile–ethyl acetate mixture (1:1, v/v). The ^{1}H NMR spectrum ($CDCl_3$) for **1**: δ 3.90 (s, 3 H), 5.10 (s, 1 H), 7.33 (m, 2 H), 7.89 (m, 2 H), 8.59 (m, 2 H). ^{1}H NMR ($CDCl_3$) for **2**: δ 8.30 (m, 2 H), 7.90 (m, 2 H), 7.30 (m, 2 H), 3.10 (s, 3 H); exact MS calcd for $C_{24}H_{18}N_4O_2$ m/e 394.1430, found 394.1428.

(B) A 5.0×10^{-3} M solution of 18DAF was purged with Ar and irradiated for 2 h. The reaction mixture was chromatographed on silica gel eluted with a benzene–acetonitrile mixture (7:3, v/v). This procedure gave 20% of diazirine **4**. This compound has the same GC retention time, mass spectrum, and molecular weight (osmetric) as 18DAF but a different behavior on TLC and a different ^{1}H NMR spectrum. **4** ($CDCl_3$): δ 8.50 (m, 2 H), 8.10 (m, 2 H), 7.38 (m, 2 H). A solution of the purified diazirine in methyl alcohol was heated at 80 °C for 20 min. Analysis of this reaction by ^{1}H NMR spectroscopy showed that **4** had been completely reconverted to 18DAF.

(C) A solution of 18DAF (250 mg in 250 mL of methyl alcohol) was purged with Ar and irradiated at 350 nm. Samples were withdrawn after 5, 10, and 20 min of irradiation and then at 30-min intervals for 6 h. The product yields were determined by analysis of the ^{1}H NMR spectra and are shown on Figure 1.

(D) Several attempts were made to isolate or characterize the unstable product from direct photolysis of 18DAF in methyl alcohol that is responsible for the absorption at δ 3.70. A solution of 18DAF (5×10^{-3} M) in methyl alcohol was irradiated to partial conversion (90 min). At this time the δ 3.70 product reaches its maximum concentration. The solvent was removed under vacuum and chromatographic separation attempted under a variety of conditions. All attempts led to destruction of the desired compound. Related efforts to purify this unstable compound by extraction met with similar failures. Attempted methylation with methyl iodide also failed.

Triplet Sensitization of 18DAF in Methyl Alcohol. A solution of 18DAF in methyl alcohol (5×10^{-3} M, 25 mg) containing 4.7×10^{-2} M benzil was purged with Ar and irradiated with light (>380 nm) until >95% 18DAF had been consumed. The ^{1}H NMR spectrum of the reaction mixture showed that 1,8-diazafluorene was the only product and that its yield was almost quantitative.

Acknowledgment. The 4,7-phenathroline-5,6-dione used in the preparation of 18DAF was a gift from CIBA-Geigy in Basel for which we are very grateful. This work was supported by a grant from the National Science Foundation and a fellowship to Y.-Z.L. from the Ministry of Education of the People's Republic of China.

Registry No. **1**, 103621-87-0; **2**, 103621-88-1; **3**, 244-50-8; 18DAF, 1807-47-2; **4**, 103621-89-2; **5**, 103621-83-6; **6**, 103639-24-3; **7**, 103621-86-9; **9**, 103621-84-7; **13**, 103621-85-8; **3** (ketone), 54078-29-4; 18DAF (carbene), 103621-90-5; 18DAF·$ZnCl_2$, 103621-82-5; DAF, 832-80-4; $ZnCl_2$, 7646-85-7; $C_6H_5CH{=}CH_2$, 100-42-5; $C_6H_5C(CH_3){=}CH_2$, 98-83-9; $H_2NNHC_6H_{11}$·HCl, 24214-73-1.

Nitronium Acetate Adducts of Furan Derivatives

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Received March 28, 1986

An improved procedure for the isolation of the main addition products of the reaction between nitronium acetate and furfural diacetate or methyl 2-furoate is described. The kinetics of the deacetylation of the diastereomeric 1,4-adducts in buffer solutions revealed a substantial primary hydrogen isotope effect. Mild acid-induced alcoholysis transformed the adducts into 2,5-dialkoxy-2,5-dihydrofurans. The reaction chemistry of the furan adducts is compared with the solvolytic pathways reported for ipso nitronium acetate adducts formed from alkylbenzenes.

During the past decade it has become a relatively routine matter to prepare and isolate ipso adducts such as **1** by nitration of the appropriate aromatic in acetic anhydride solvent systems.[1] The current view is that such adducts

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