

Wavelength-Dependent Photochemistry of a Diazo Compound: Irradiation of 9-Diazo-1,8-diazafluorene with Ultraviolet or Visible Light

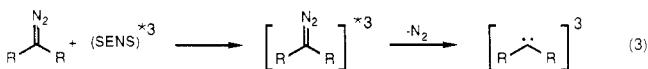
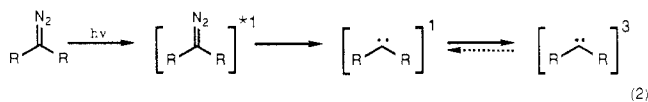
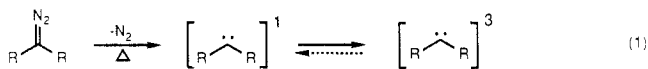
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The photochemistry of 9-diazo-1,8-diazafluorene (18DAF) depends on the wavelength of the irradiating light. When photolyzed at ca. 310 nm, into a $\pi-\pi^*$ absorption band, excited 18DAF rearranges to a diazirine and loses nitrogen to form the carbene 1,8-diazafluorenylidene (18FL) exclusively in the singlet state. However, when 18DAF is photolyzed at ca. 420 nm, into the $n-\pi^*$ band, no diazirine is formed, but triplet 18FL is formed directly along with the singlet, and the quantum yield for reaction is reduced ca. 12-fold when compared with the UV photolysis.

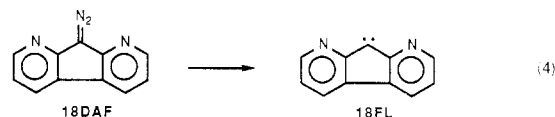
The properties of carbenes continue to spark the imagination of chemists.¹ These extremely reactive and useful intermediates are formed most commonly by thermolysis or photolysis of corresponding diazo compounds. It has usually been assumed that spin is conserved in these reactions. That is, thermolysis of a diazo compound (ground-state singlet) leads to loss of nitrogen and generation of the carbene also in a singlet state. These singlet carbenes may (and often do) intersystem cross to a lower energy triplet before they are consumed in bimolecular reactions (eq 1). Similarly, it is commonly assumed that direct irradiation of diazo compounds gives their electronically excited singlet states, which rapidly lose nitrogen with spin conservation to form singlet carbenes (eq 2). In contrast, reactions promoted by triplet sensitization are thought to proceed through the triplet state of diazo compounds to give directly triplet carbenes that do not have a singlet carbene precursor (eq 3). The ability to generate carbenes in these "spin-specific" ways has facilitated the assignment of appropriate properties to their singlet and triplet states.



Diazo compounds with aromatic hydrocarbon substituents generally exhibit two well-separated optical-absorption systems. There are intense UV bands associated with the $\pi-\pi^*$ transitions of the aromatic chromophore and a weaker band in the visible region crudely attributable to an $n-\pi^*$ transition of the diazo group.² Little consideration has been given to the possibility that the reaction sequence leading to carbene formation could depend on whether the diazo compound is excited with UV or visible light.³ In part, this issue was ignored because of the

common prejudice for wavelength-independent photochemistry (by analogy to Kasha's and Vavilov's rules for emission).⁴ And in part, this question was not studied because suitable systems to reveal wavelength-dependent behavior were not readily available.

Recently we reported on the photochemistry of 9-diazo-1,8-diazafluorene (18DAF).⁵ Irradiation of this diazo compound in inert solvents leads to loss of nitrogen and formation of 1,8-diazafluorenylidene (18FL) (eq 4). The



chemical properties of 18FL are unusual when compared with those of fluorenylidene (FL) and other structurally related carbenes.^{1,6} In particular, singlet 18FL is more reactive than singlet FL in its addition to olefins to form cyclopropanes. Thus, despite fast and irreversible intersystem crossing to its triplet ground state, the first-formed singlet state of 18FL can be trapped at high olefin concentration. This permits experiments to probe for a wavelength dependence in the photochemistry of the diazo compound. We report herein that irradiation of 18DAF with UV light gives the carbene initially exclusively in its singlet state (eq 2), but irradiation of this diazo compound with visible light gives some triplet 18FL that does not have a singlet-carbene precursor.

Results

The electronic-absorption spectrum of 18DAF in hexafluorobenzene (HFB) solution is shown in Figure 1 (this solvent was chosen for its relative inertness toward reaction with carbenes, essentially comparable results are obtained from studies in benzene solution).⁷ There are two absorption features that are well-separated and easily observed. The first is a strong UV band with maximum absorption at 312 nm and a maximum extinction coefficient of $12000 \text{ cm}^{-1} \text{ M}^{-1}$. The second feature is a much less intense band with a maximum at 410 nm and an extinction coefficient of only $60 \text{ cm}^{-1} \text{ M}^{-1}$. These absorptions are assigned crudely as $\pi-\pi^*$ and $n-\pi^*$ transitions, respectively, on the basis of their extinctions and by analogy with related chromophores.²

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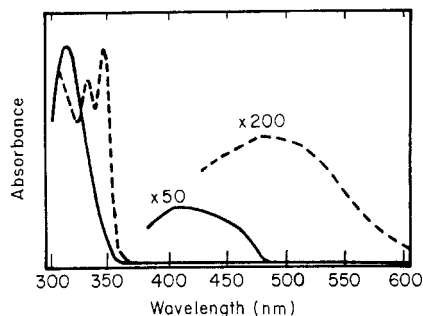
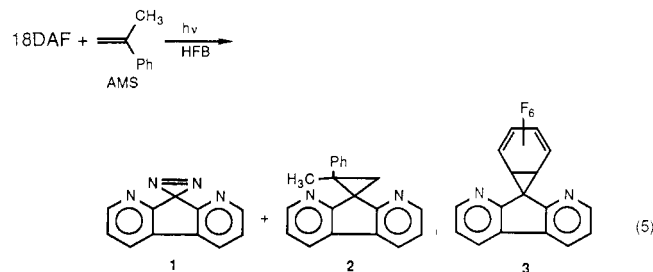


Figure 1. Absorption spectra of 18DAF (solid line) and DAF (broken line) in HFB solution.

The absorption spectrum of 18DAF is remarkable when compared with that for 9-diazafluorene (DAF), the "parent" compound, shown also on Figure 1. In particular, the visible transition of 18DAF shows a hypsochromic shift of nearly 100 nm. We were concerned that this large shift signaled isomerization of 18DAF to a triazole.⁸ However, the ¹H NMR and IR spectra of 18DAF are consistent only with the diazo structure, and its UV spectrum does not change with temperature as it might if there were two or more isomers in equilibrium. Additionally, the UV spectrum of 9-diazo-3,6-diazafluorene,⁹ which cannot tautomerize to a triazole, is virtually identical with that of 18DAF. Finally, MINDO/3 calculations, which accurately predict the closed form for 2-pyridyldiazomethane, indicate that 18DAF will exist as the diazo isomer. Thus, the shift of the $n-\pi^*$ transition to higher energy for 18DAF must be a consequence of an electronic perturbation by its ring nitrogen atoms.

Irradiation of 18DAF in HFB containing α -methylstyrene (AMS) at 310 ± 10 nm gives three major products. These are the 1,2-diazirine 1 formed from photoisomerization of 18DAF, the cyclopropane 2 from addition of 18FL to the styrene,^{5,10} and norcardiene 3 formed from addition of the carbene to HFB (eq 5).⁷ The relative yields



of these products depend on the concentration of AMS and on the extent of consumption of 18DAF. The first observation is self-explanatory; the second is due to secondary photolysis of diazirine 1 at this wavelength. Consequently, all photolyses were run only to ca. 15% conversion so that the diazirine never absorbs a significant amount of light, and the complications arising from its irradiation are avoided. Typical product compositions from experiments run under these conditions are shown in Table I.

Irradiation of 18DAF in HFB solution containing AMS at 420 ± 20 nm instead of in the UV region gives a different result. Under these conditions the carbene derived cyclopropane 2 and norcardiene 3 are still formed, but there is no detectable photoisomerization to diazirine 1. We

Table I. Yield Ratios and Selectivities of the Products from the Irradiation of 18DAF

irradiation wavelength, nm	[AMS], M	conversion of 18DAF, %	yield ratio	stereoselectivity <i>R</i>
310	2.0	10	1.4 ^a	0.48
	3.4	12	2.3 ^a	0.58
	4.3	10	4.5 ^a	0.67
	5.8	16	9.0 ^a	0.73
	7.7	18	89 ^b (8.8) ^c	0.85
	7.7	72	88 ^b (8.1) ^c	0.90
420	2.0	15	1.5 ^a	0.30
	3.4	16	2.5 ^a	0.36
	4.3	20	4.8 ^a	0.44
	5.8	16	9.4 ^a	0.47
	7.7	13	92 ^{b,d}	0.59
	7.7	67	89 ^{b,d}	0.60

^a Ratio of the yield of cyclopropane 2 to norcardiene 3 determined by gas chromatography. ^b Yield of the cyclopropane 2 (%). ^c Yield of the diazirine 1 (%). ^d No diazirine 1 detected.

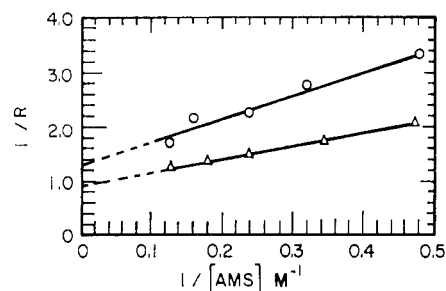


Figure 2. Double-reciprocal plot of stereospecificity (*R*) against α -methylstyrene concentration for irradiation of 18DAF in HFB solution at 310 nm (triangles) and at 420 nm (circles).

eliminated the possibility that the diazirine was somehow being destroyed under these conditions by showing that authentic samples survive the irradiation. Evidently, isomerization to 1 occurs from an upper excited state of 18DAF that is not populated by visible-light irradiation. This was the first indication of wavelength-dependent behavior in the photolysis of 18DAF. Typical product compositions from experiments run under these conditions are shown also in Table I.

The stereochemical outcome of olefin cyclopropanation by carbenes provides the most readily interpreted evidence for the spin multiplicity of the reacting state. The Skell-Woodworth hypothesis, wherein singlet carbenes give cyclopropanes with retention of olefin stereochemistry and cyclopropanes formed from triplet carbenes have randomized stereochemistry, is valid in every example studied.^{1,11} For the case of 18DAF, we found that triplet-sensitized carbene generation always gives completely nonstereospecific cyclopropanation, but direct irradiation gives cyclopropanes where the degree of retention depends upon the olefin concentration.⁵ This behavior provides an opportunity to study the effect of photolysis wavelength on the multiplicity of the first-formed carbene state.

In these experiments we chose (*E*)- β -deuterio- α -methylstyrene as the probe for the cyclopropanation reaction. This olefin provides several key advantages. The most important are that it gives a high (nearly quantitative) yield of the cyclopropane from the triplet carbene, the cyclopropane stereoisomers differ only by the position of deuteration, and the stereochemical orientation of the cyclopropane can be easily determined from its ¹H NMR spectrum. For this analysis we define *R* as the degree of

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Table II. Irradiation of DAF in the Presence of α -Methylstyrene

irradiation wavelength, nm	[AMS], M	conversion of DAF, %	stereoselectivity <i>R</i>
310	2	66	0.19
	4	60	0.30
	6	55	0.40
525	7.7	60	0.65
	2	50	0.22
	4	60	0.34
	6	55	0.42
	7.7	45	0.55

Table III. Quantum Yields for Photolysis of Diazo Compounds

diazo compd	irradiation wavelength, nm	$\Phi_{-N_2}^a$	Φ_{diaz}^b
18DAF	310	0.12 \pm 0.02	0.04
18DAF	420	0.01 \pm 0.003	ND ^c
DAF	310	0.32	ND
DAF	525	0.04	ND
Ph ₂ CN ₂	310	0.71 ^d	ND
Ph ₂ CN ₂	525	0.06	ND

^aQuantum yield for loss of diazo compound. ^bQuantum yield for formation of diazirine 1. ^cUnobservable by ¹H NMR spectroscopy. ^dPreviously reported to be 0.78 at 288 nm in methanol: Kirmse, W.; Horner, L. *Justus Liebigs Ann. Chem.* 1959, 634, 34.

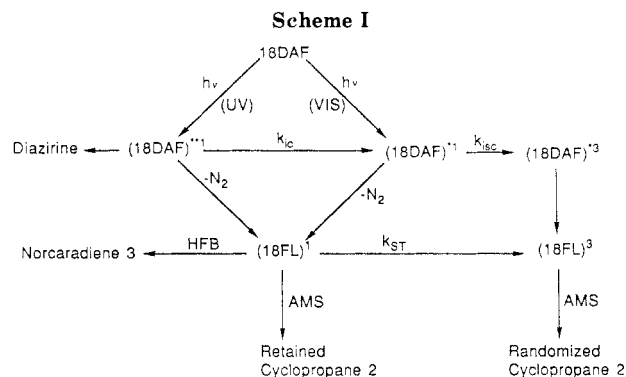
olefin configuration retained in the cyclopropane according to eq 6. Thus, *R* ranges from 1.0 for complete retention to 0.0 for total randomization of the olefin configuration.

$$R = (\text{retained} - \text{inverted}) / (\text{retained} + \text{inverted}) \quad (6)$$

Shown in Figure 2 are double-reciprocal plots of *R* against the concentration of AMS for irradiation of 18DAF at 310 and at 420 nm in HFB solution. Several facts are apparent from inspection of these plots. First, *R* is greater for UV photolysis than it is for visible-light irradiation at all AMS concentrations. Second, at extrapolated infinite styrene concentration (the *y* intercept of the plots), *R* is within experimental uncertainty of 1.0 (complete retention) for the 310-nm photolysis, but irradiation with visible light results in cyclopropanation with incomplete retention of olefin configuration even at this limit. Finally, the slopes of these lines depend on the wavelength of irradiation. It is possible to interpret these findings more precisely once a mechanism for this reaction is postulated. This analysis is deferred to the Discussion.

For comparison, we examined the photolysis of the parent diazo compound (DAF) at 310 (π - π^*) and 525 nm (n - π^*) in the presence of high concentrations of AMS. The results are shown in Table II. For this case, *R* is smaller than it is for 18DAF at the lower AMS concentrations because less of the singlet carbene is trapped before intersystem crossing to the ground-state triplet.^{5,6} However, UV or visible-light irradiation of DAF uniformly give the same *R*, and extrapolation to infinite olefin concentration shows greater than 94% retention in both cases.

There is a third effect of irradiation wavelength on the chemistry of 18DAF, one that is also present in other diazo compounds. Quantum yields for consumption of 18DAF are shown in Table III. These values were measured by comparison with both ferrioxalate¹² and Aberchrome¹³



actinometers. The consumption of the diazo compound was monitored by IR-absorption spectroscopy. In the case of the UV irradiation of 18DAF, this measurement reports both isomerization to diazirine 1 and loss of nitrogen to form 18FL. These processes were separated by measuring the chemical yields (Table I) of 1 and 3 under these conditions. It is apparent from inspection of Table III that irradiation with visible light gives much less efficient reaction of 18DAF than does UV photolysis. The quantum efficiency for carbene formation is ca. 12 times greater at 310 nm than it is at 425 nm. Approximately this same behavior is seen in the photolysis of DAF (310 vs. 525 nm) and for diphenyldiazomethane (310 vs. 525 nm). These observations demonstrate that the thermally equilibrated lowest excited singlet state of these diazo compounds cannot be the sole source of carbene.

Discussion

The key result of this investigation is finding wavelength-dependent photochemistry for 18DAF. This behavior is observed in three independent experiments. First, isomerization to the diazirine occurs only for UV irradiation. Second, visible but not UV photolysis gives nonstereospecific cyclopropanation of α -methylstyrene at extrapolated infinite olefin concentration. Finally, the quantum yield for nitrogen loss shows a dramatic wavelength dependence. This last effect is observed also for DAF, but the other effects are not apparent in this case. Our objective is to present a mechanistic scheme that accounts for these results and to attempt to relate the behavior of 18DAF to electronic perturbation by its ring nitrogen atoms.

The mechanistic hypothesis outlined in Scheme I is in accord with all of the experimental observations. Irradiation of 18DAF with UV light gives an upper excited singlet state of the diazo compound 18DAF**1. This species can isomerize to the diazirine or lose nitrogen to form the singlet carbene 18FL¹ or return to the ground state. Visible-light irradiation forms a lower energy singlet state of the diazo compound 18DAF*1 that can lose nitrogen or return to the ground state or intersystem-cross to the triplet diazo compound 18DAF*3. Loss of nitrogen from 18DAF*3 gives triplet carbene 18FL³ that does not have a singlet-carbene precursor. Internal conversion of 18DAF**1 to 18DAF*1 (*k_{ic}*) may contribute to the non-reactive consumption of the upper state. However, because the quantum yield for nitrogen loss from 18DAF*1 is so much less than from 18DAF**1 (Table III), diagnostic direct formation of 18FL*3 by this route is experimentally undetectable even at extrapolated infinite AMS concentration.

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The slope and intercept of the double-reciprocal plots shown in Figure 2 can be interpreted quantitatively within the mechanistic hypothesis of Scheme I. Solution of the kinetic network (described in the supplementary material) for this scheme gives eq 7 where k_{HFB} and k_{AMS} are the rate constants for reaction of 18FL^1 with HFB and AMS, respectively, and d_{AMS} and MW_{AMS} are the density and molecular weight of AMS (HFB). The linear response of $1/R$ to $1/[\text{AMS}]$ is predicted by this analysis. The ratio $k_{\text{HFB}}/k_{\text{AMS}}$ was calculated from competition experiments.

$$\frac{1}{R} = 1 + \left[\frac{f_3}{f_1}(S) \right] + \left[K + \frac{f_3}{f_1}[M] \right] \frac{1}{[\text{AMS}]} \quad (7)$$

$$\text{where } S = \left[1 - \frac{k_{\text{HFB}}}{k_{\text{AMS}}} \left(\frac{d_{\text{AMS}} MW_{\text{AMS}}}{d_{\text{HFB}} MW_{\text{HFB}}} \right) \right]$$

$$K = f(k_{\text{st}}, k_{\text{AMS}})$$

$$M = f(k_{\text{st}}, k_{\text{HFB}}, k_{\text{AMS}})$$

Of primary interest is f_3/f_1 , the ratio of the yield for direct (no singlet-carbene precursor) formation of 18FL^3 to that for direct formation of the singlet carbene. This parameter can be calculated from the intercepts of the lines shown in Figure 2. For 18DAF the results depend on the wavelength of irradiation. Photolysis at 310 nm gives f_3/f_1 statistically indistinguishable from zero. That is, all of the triplet carbene that is formed in this reaction has a singlet-carbene precursor. However, for irradiation of 18DAF at 420 nm, $f_3/(f_3 + f_1) = 0.35 \pm 0.08$. Thus for visible-light photolysis, ca. 35% of the 18DAF that loses N_2 gives triplet carbene that is not formed from the singlet. This direct formation of 18FL^3 signals intersystem crossing of 18DAF^{*1} before N_2 loss. In contrast, irradiation of DAF either at 310 nm or at 525 nm gives the same result; f_3/f_1 is within experimental error of zero in both cases. Thus, under all conditions, every FL^3 is formed from a FL^1 precursor. Intersystem crossing of DAF^{*1} must be insignificant.

Lastly, it is important to attempt to recognize the fundamental factors that make the photochemistry of 18DAF different from DAF and other diazo compounds that have been studied. It is not possible to reach sure and certain conclusions with the available data, but some generalization is warranted. It seems clear that an important difference between DAF^{*1} and 18DAF^{*1} is the rate constant for intersystem crossing to the triplet diazo compound (k_{isc}) relative to loss of nitrogen to give the singlet carbene. For DAF, k_{isc} is of negligible importance, but for 18DAF it plays a significant role. This could result either from an increase in k_{isc} or from a decrease in the rate constant for nitrogen loss (or both). The first possibility is consistent with the large hypsochromic shift observed in the absorption spectrum of 18DAF. Rates of intersystem crossing are often controlled by the relative energies of electronic states of different configuration (El-Sayed's rules).¹⁴ The shift in the $n-\pi^*$ absorption band may signal a reordering of states to one more prone toward intersystem crossing. The second possibility is consistent with the high activation barrier for N_2 loss observed in the thermolysis of 18DAF.⁵ If this reaction is similarly slowed in the excited state, then formation of 18DAF^{*3} could be important even if k_{isc} is unchanged. This explanation is attractive because it may also account for diazine formation from 18DAF^{*1} .

Whatever the actual cause for the unusual behavior of 18DAF might be, the fact of its existence should serve as

a warning in the mechanistic interpretation of the photochemistry of diazo compounds. Direct irradiation of diazo compounds does not lead necessarily to primary formation of a carbene exclusively in its singlet spin state.

Experimental Section

General Procedures. Routine ^1H NMR spectra were recorded on a Varian XL-200 (200 MHz, FT) or General Electric QE-300 (300 MHz, FT) spectrometer in chloroform-*d* solution with 0.2% TMS as the internal standard. Mass spectra were obtained with Varian MAT CH-5 and 731 mass spectrometers. UV-visible absorption spectra were recorded on a Perkin-Elmer 552 spectrophotometer. Infrared spectra were obtained with an IBM IR-32 instrument, and 18DAF was prepared as previously described.⁵ Photolyses were carried out in a light box equipped with a 450-W medium-pressure mercury lamp and solution or glass filters that isolated bands centered at 310, 336, 420, or 525 nm.¹²

Variable-Temperature UV Spectra of 18DAF. 18DAF (10.0 mg) was dissolved in 5.0 mL of diphenyl ether in a Pyrex cuvette and heated to five preset temperatures between 25 and 125 °C. The UV spectrum was recorded at each temperature, and then the IR spectrum of the sample was rerecorded at room temperature. Neither the UV nor the IR spectra showed any significant change or effect of temperature.

Photolysis of 18DAF in HFB Containing (*E*)- β -Deuterio- α -methylstyrene. Five solutions of 18DAF (5×10^{-3} M) in hexafluorobenzene containing respectively 2.0, 3.4, 4.3, 5.8, and 7.7 M (neat) (*E*)- β -deuterio- α -methylstyrene were purged with N_2 and irradiated for 70 min at ca. 310 nm. The ^1H NMR spectrum of each reaction mixture was recorded after the solvent and most of the unreacted styrene were removed under vacuum. The spectra showed unreacted diazo compound, diazine 1,⁵ cyclopropane 2,⁵ and norcaradiene 3 (identified by its NMR and mass spectra; see below). The spectrum of the residual deuterated methylstyrene showed that it had not been isomerized by the reaction or the workup. The yields of the cyclopropane isomers were determined from integration of the peak at 2.5 ppm assigned to the *Z* isomer and the absorption at 2.8 ppm of the *E* isomer. In a similar experiment, five samples of 18DAF (5.0×10^{-3} M) containing the deuterated α -methylstyrene were purged with nitrogen, irradiated at ca. 420 nm, and then worked up and analyzed as above. Control experiments showed that the cyclopropane is not isomerized after it is formed under these conditions, nor is the α -methylstyrene isomerized significantly during the reaction. Spectra of 3: ^1H NMR (CDCl_3) δ 7.44 (2 H, m), 8.02 (2 H, m), 8.60 (2 H, m); MS, *m/e* 352.0; ^{19}F NMR (CDCl_3 , C_6F_6) = -163 ppm δ -153.3 (m, 2 F), -151.1 (m, 2 F), -122.1 (m, 2 F); exact mass calcd for $\text{C}_{17}\text{H}_6\text{N}_2\text{F}_6$ 352.0428, found 352.0431.

Irradiation of DAF in HFB Containing (*E*)- β -Deuterio- α -methylstyrene. Four samples of DAF (5×10^{-3} M) were prepared in hexafluorobenzene containing 2, 4, 6, and 7.7 M (neat) (*E*)- β -deuterio- α -methylstyrene, respectively. The samples were purged with nitrogen and then irradiated for ca. 70 min at ca. 310 nm. The ^1H NMR spectrum of each reaction sample was recorded after the solvent and most of the styrene were removed under vacuum. The expected cyclopropane⁶ is formed nearly quantitatively in all cases. The isomer ratio for the cyclopropanes was calculated from the peak at 2.02 ppm assigned to the *Z* isomer and the peak at 2.40 ppm characteristic of the *E* compound. In a similar experiment, four samples of DAF (5.0×10^{-3} M) containing the deuterated α -methylstyrene were purged with nitrogen, irradiated at ca. 525 nm, and then worked up and analyzed as above.

Quantum Yields for Reaction of Diazo Compounds. Ferrioxalate and Aberchrome¹³ (AC540) actinometers were employed to measure the quantum yields for disappearance of DAF, 18DAF, and diphenyldiazomethane. A 1.5 M solution of $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$ was prepared for measurements at 525 nm, and a 0.06 M solution was used for 310- and 425-nm measurements. A 5×10^{-3} M solution of the AC540 (A form) was prepared for 310-nm measurements, and a 5×10^{-4} M solution of the B form of Aberchrome was prepared for the 425- and 525-nm measurements. The two actinometers gave nearly the same measured light intensities at ca. 310, ca. 420, and 525 nm. The diazo compounds (5×10^{-3} M) were dissolved in toluene and irradiated simulta-

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neously with the actinometer at the appropriate wavelength. The conversion of the diazo compound was monitored by IR spectroscopy. The results are summarized in Table III.

Measurement of $k_{\text{AMS}}/k_{\text{HFB}}$ for 18DAF. The ratio of the reaction rate constants was obtained from the analysis of the yield ratio of the products. The calculation is based on the following equation:

$$\frac{k_{\text{AMS}}}{k_{\text{HFB}}} = \frac{(\text{yield of } 2) \times [\text{HFB}]}{S \times (\text{yield of } 3) \times [\text{AMS}]}$$

where S is obtained from Table I and is the fraction of the cyclopropane that comes from the singlet carbene.

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Registry No. 1, 103621-89-2; 2, 103621-86-9; 3, 109929-84-2; 18DAF, 1807-47-2; 18FL, 103621-90-5; HFB, 392-56-3; AMS, 98-83-9; (*E*)- β -deuterio- α -methylstyrene, 69912-51-2.

Supplementary Material Available: Description of the solution of the kinetic network for Scheme I (7 pages). Ordering information is given on any current masthead page.

Formation of 4-Nitrocyclohexa-2,5-dienols by Addition of Organolithium Reagents to 4-Alkyl-4-nitrocyclohexa-2,5-dienones¹

Alfred Fischer* and S. Sankararaman

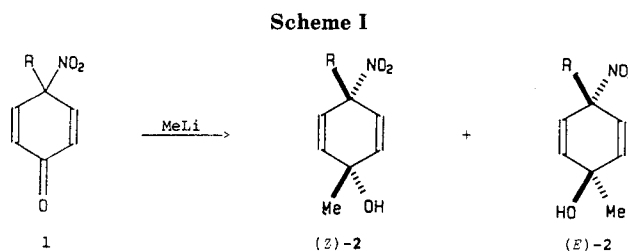
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Addition of methyllithium to 4-alkyl-4-nitrocyclohexa-2,5-dienones **1a-d** (alkyl = Me, Et, *i*-Pr, *t*-Bu) to 2,6-dichloro- and 2,6-dibromo-4-methyl-4-nitrocyclohexa-2,5-dienone, and to 4a-nitro-2-oxo-2,4a,5,6,7,8-hexahydronaphthalene gives the corresponding dienols **2a-d**, **4e** and **4f**, and **7g**, generally as a pair of diastereomers. Addition of methyl lithioacetate to the same substrates gives dienols **8a-d**, **5e** and **5f**, and **7h**. Addition of substituted methyllithiums (XCH₂Li, X = CN, CONH₂, CONMe₂, COMe, SMe, SPh, SOMe, SO₂Me, SiMe₃, PSMePh, PSPPh₂), 2-lithio-1,3-dithiane, or lithium phenylacetylide to **1a** gives the dienols **9i-u**.

Nitronium acetate adducts (nitrocyclohexadienyl acetates), in which the nitro group is attached to an activated substituted site, are often formed when arenes and their derivatives are nitrated in acetic anhydride.²⁻⁴ With appropriate substrates good yields of adducts are obtained, but as a means of preparing such adducts direct nitration suffers from some inherent limitations. Thus, the ipso position to which the nitronium ion is to be added must be relatively activated; regioisomers may be formed in the ipso nitration;⁵⁻⁸ and some substituents, such as those containing sulfur, phosphorus, or silicon are sensitive to the nitration conditions.⁹⁻¹¹

Myhre and co-workers developed an efficient process for the synthesis of ipso nitration products in which a 4-alkyl-4-nitrocyclohexa-2,5-dienone is reduced with sodium borohydride in methanol to form the corresponding 4-alkyl-4-nitrocyclohexadienol.¹² They also showed that ad-



a, R = Me. b, R = Et. c, R = *i*-Pr. d, R = *t*-Bu.

dition of methyllithium to 4-methyl-4-nitrocyclohexa-2,5-dienone (**1a**) gave an excellent yield of 1,4-dimethyl-4-nitrocyclohexa-2,5-dienol (**2a**). We have extended the latter reaction to the preparation of 4-alkyl-4-nitrocyclohexa-2,5-dienols from a number of different 4-alkyl-4-nitrocyclohexadienones using methyllithium and a series of substituted alkyl lithium reagents. Our results demonstrate that this is a very effective method for the synthesis of such cyclohexadienols.

Results and Discussion

Preparation of 4-Nitrocyclohexadienones. Methods for the preparation of 4-methyl-, 4-ethyl-, and 4-isopropyl-4-nitrocyclohexa-2,5-dienones and of 2,6-dichloro- and 2,6-dibromo-4-methyl-4-nitrocyclohexadienones are well established.^{12,13} Higher yields of dienone are obtained on nitration of the aryl acetate rather than the phenol.¹² However, we have found that nitration of the phenol with nitric acid and trifluoroacetic anhydride in ether is a particularly simple way of making dienones. Although the yields of dienone is inferior to that obtained by nitration of the aryl acetate with nitric acid in acetic anhydride, this

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