

## Photochemistry of 9-Diazo-3,6-diazafluorene: Through-Space or Through-Bond Transmission of Electronic Effects

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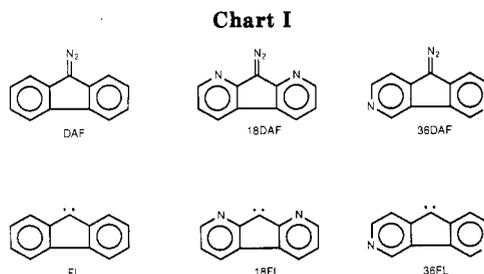
*Received March 19, 1987*

Irradiation of 9-diazo-3,6-diazafluorene (36DAF) in hydrocarbon solvents gives 3,6-diazafluorenylidene (36FL) by loss of  $N_2$  and the isomeric diazirine 1 by valence tautomerization. The chemical and physical properties of 36DAF are compared with those of the positional isomer 9-diazo-1,8-diazafluorene (18DAF) and with its "parent", 9-diazafluorene (DAF). Similarly, 36FL is compared with the isomeric 1,8-diazafluorenylidene (18FL) and with fluorenylidene (FL). In most respects, the properties of the 3,6-positional isomers are very similar to those of the 1,8-positional isomer, but they are quite different from those of FL and of DAF. These findings show that the mechanism for transmission of electronic perturbation by the ring-nitrogen atoms is through-bonds rather than through-space. Irradiation of 36DAF in methyl alcohol leads to chemical transformations not previously observed in related diazo compounds. This behavior is traced to an unusual photoactivated electron-transfer reaction.

A topic of long-standing interest in chemistry is the mechanism for transmission of electronic effects from a remote perturbing group to a sensitive reaction center.<sup>1</sup> Two nonexclusive hypotheses have been advanced. The first involves through-space transmission where actual overlap or interaction (dipole-dipole, for example) between electrons of the perturbing group and the reaction center is required. The second mechanism operates through the electrons in intervening bonds. This path is frequently invoked to explain effects observed in conjugated  $\pi$ - or extended  $\sigma$ -bonded systems.

The reactions of carbenes are particularly sensitive to electronic perturbation. One reason for this is that small shifts in energy may change the spin multiplicity of the ground state. For example, theory predicts and experiment confirms that methylene ( $CH_2$ ; the "parent" of all carbenes) has a triplet ground state<sup>2</sup> located ca. 9 kcal/mol ( $\Delta G_{st}$ ) below the lowest energy singlet state. Substitution of  $\pi$ -electron-donating groups for the hydrogens (methoxy or halogen, for example) on methylene inverts this order and profoundly changes the chemical properties of the carbene.<sup>3</sup> Similarly, fluorenylidene (FL, see Chart I) is a triplet in its ground state ( $\Delta G_{st} \approx 2$  kcal/mol),<sup>4</sup> but addition of electron-donating methoxy groups makes the singlet of 3,6-dimethoxyfluorenylidene the ground state.<sup>5</sup>

Recently we reported the results of the investigation of 9-diazo-1,8-diazafluorene (18DAF).<sup>6,7</sup> 18DAF is unusual in comparison with related diazo compounds. For example, it is not decomposed by strong mineral or Lewis acids, and its thermal decomposition requires a much higher temperature than does DAF. The photochemistry of 18DAF is unusual too. Irradiation with UV light gives 1,8-diazafluorenylidene (18FL) and causes isomerization to the diazirine. No diazirine is formed when 18DAF is photolyzed with visible light, and, under these conditions, some 18FL is formed directly in its triplet ground state.



**Table I. Chemical and Spectroscopic Properties of DAF, 18DAF, 36DAF, FL, 18FL, and 36 FL**

	DAF	18DAF	36DAF
IR (CHCl <sub>3</sub> ), cm <sup>-1</sup>	2058	2091	2076
UV (benzene), $\lambda_{max}$ (log $\epsilon$ )	347 (4.04), 480 (1.56)	312 (4.08), 413 (1.78)	328 (4.03), 407 (1.70)
<sup>1</sup> H NMR (CDCl <sub>3</sub> ), $\delta$	7.3, 7.5, 7.95	7.25, 8.12, 8.48	7.54, 8.65, 9.32
<sup>13</sup> C NMR (C <sub>6</sub> ) (CD <sub>3</sub> OD), $\delta$	64.0	65.1	67.1
<sup>15</sup> N NMR (CDCl <sub>3</sub> ), $\delta$	440 (N <sub>11</sub> ), <sup>a,b</sup> 286 (N <sub>10</sub> )	400 (N <sub>11</sub> ), <sup>b</sup> 262 (N <sub>10</sub> ), 283 (N <sub>1,8</sub> )	
pK <sub>b</sub> (CH <sub>3</sub> OH)		11.2	9.4
ESR (4 K, MTHF)			
	FL	18FL	36FL
D , cm <sup>-1</sup>	0.408	0.442	0.438
E , cm <sup>-1</sup>	0.0283	0.029	0.0306

<sup>a</sup> Previous measurement by D. G. Morris and A. M. Murray (*J. Chem. Soc., Perkin Trans. 2* 1976, 1579): 441.0 (N-11), 287.0 (N-10). <sup>b</sup> Referenced by substitution to nitromethane used as secondary reference, set 380 ppm relative to NH<sub>3</sub> (liquid). Experiment performed on GN300WB NMR spectrometer.

The triplet of 18FL behaves in an ordinary manner, but the singlet is exceptional. For example, the singlet carbene inserts into the carbon-hydrogen bonds of cyclohexane hundreds of times faster than does singlet FL. In fact, singlet 18FL is such a powerful electrophile that it adds to benzene or styrene with approximately the same rate constant. We speculated that the unusual properties of 18DAF and 18FL might be either a consequence of the unique spatial arrangement of the three pairs of non-bonding electrons (one pair in the in-plane  $\sigma$ -orbital of the carbene carbon and one pair in each of the ring-nitrogen atoms) or a consequence of the through-bond perturbation of electronic configuration. We undertook the investigation of 3,6-diazafluorenylidene (36FL) and 9-diazo-3,6-diazafluorene (36DAF) to examine further the mechanism for

(1) Gleiter, R. *Angew. Chem., Int. Ed. Engl.* 1974, 13, 696. Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum: New York, 1975, Chapter 3.

(2) Feller, D.; McMurchie, L. E.; Borden, W. T.; Davidson, E. R. *J. Chem. Phys.* 1982, 77, 6141. Leopold, D. G.; Murray, K. K.; Lineberger, W. C. *J. Chem. Phys.* 1984, 81, 1048.

(3) Moss, R. A. *Acc. Chem. Res.* 1980, 13, 58.

(4) Grasse, P. B.; Brauer, B.-E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* 1983, 105, 6833. 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.

(5) Chuang, C.; Lapin, S. C.; Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* 1985, 107, 4238.

(6) Li, Y.-Z.; Schuster, G. B. *J. Org. Chem.* 1986, 51, 3804.

(7) Li, Y.-Z.; Schuster, G. B. *J. Org. Chem.*, in press.

transmission of the electronic perturbation.

## Results

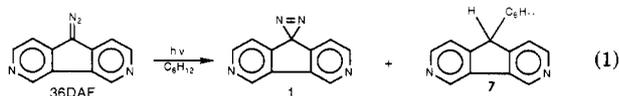
**1. Spectroscopic Properties of 36DAF.** The synthesis of 36DAF was modeled after that of 18DAF and is fully described in the Experimental Section. We compared the IR, NMR, and UV-vis spectra of 36DAF with those of DAF and 18DAF. The data are summarized in Table I. Of particular interest are those features that are dependent on the electron density at the diazo group. For example, it is generally observed that electron-withdrawing groups on phenyl-substituted diazo compounds raise the frequency of their strong, characteristic band at ca. 2000  $\text{cm}^{-1}$ .<sup>8</sup> This effect operates strongly for 18DAF and somewhat less so for 36DAF. Similarly, the energy of the  $n-\pi^*$  optical transition is sensitive to electron withdrawal and "stabilization" of the nonbonding electron pair. This effect is evident also for 18DAF and 36DAF. In comparison with DAF, the maxima of the  $n-\pi^*$  transition are blue-shifted by ca. 70 nm. These results and the other data in Table I point to a qualitatively similar perturbation by the ring nitrogens for both 18DAF and 36DAF.

**2. Thermal Reactions of 36DAF.** In contrast to 18DAF, the thermal stability of 36DAF is approximately the same as that for DAF. For example, 18DAF has a half-life of at least 2 days in diphenyl ether at 140 °C. Under these conditions, DAF has a half-life of ca. 30 min and for 36DAF this value is ca. 2 h. Both 18DAF and 36DAF are much more stable in acidic solution than DAF; they can be recovered unchanged from solutions containing strong protic or Lewis acids.

There is a significant difference in the basicity of 18DAF and 36DAF. The  $\text{p}K_b$  values for these diazo compounds were determined by comparison with a series of standard bases with bromophenol blue as the indicator. A plot of the absorption of the indicator against the reference bases gives  $\text{p}K_b$  values for 18DAF and 36DAF equal to 11.2 and 9.4, respectively.<sup>8</sup> Thus, 36DAF is a considerably stronger base than is 18DAF. Both the reduced basicity and increased thermal stability of 18DAF indicate some proximity-dependent interaction between the diazo group and the pyridine-like ring-nitrogen atoms. The difference in basicity appears to control the photochemistry of 36DAF in alcoholic solvents (see below).

**3. Photolysis of 36DAF in Frozen Media.** Irradiation of 36DAF in a 2-methyltetrahydrofuran glass at 4 K gives a paramagnetic species characterized by its ESR spectrum as triplet 3,6-diaza-9-fluorenylidene (<sup>3</sup>36FL). This spectrum is stable for at least 2 h at low temperature, but it disappears when the sample is warmed to room temperature and then refrozen. The zero field parameters (Table I) were calculated in the usual way from the ESR spectrum. These values show that <sup>3</sup>36FL has a geometry and electronic configuration similar to those of both triplet fluorenylidene and to <sup>3</sup>18FL.<sup>9</sup>

**4. Direct Photolysis of 36DAF.** Irradiation of 36DAF (350 nm) in cyclohexane gives 9-cyclohexyl-3,6-diazafluorene (85%) and valence isomerization to diazirine 1 (10%), eq 1. The absence of radical dimerization products



in this reaction indicates that the solvent-insertion product

(8) Gordon, A. R.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972.

(9) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance*; Chapman and Hall: London, 1986; Chapter 10.

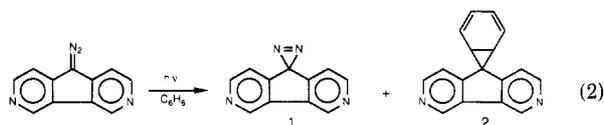
**Table II. Products from Irradiation of Diazo Compounds in Benzene with  $\alpha$ -Methylstyrene**

diazo compound	wave-length, nm	[AMS], M	product yields, %		$R^a$
			cyclopropane	norcaradiene	
36DAF	310	7.7 (neat)	75	NA	0.94
36DAF	310	1.0	20	70	<0.05
36DAF	420	7.7	86	NA	0.63
36DAF	420	3.0	60	22	0.31
36DAF (Sens)*	1.0		96	<5	0.00
18DAF	310	7.7	87	NA	0.90
18DAF	420	7.7	90	NA	0.60
18DAF	310	1.0	10	70	<0.05
DAF	310	7.7	95	NA	0.65
DAF	310	0.5	90	<5	0.15

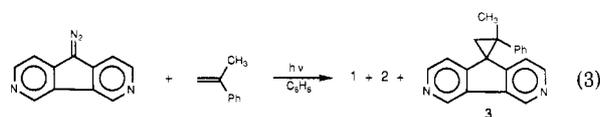
<sup>a</sup> Retention ( $R$ ) is defined as [(retained - inverted)/(retained + inverted)].

originates with the singlet carbene. This was confirmed for 18FL by isotope tracer studies. In contrast, irradiation of DAF in cyclohexane gives products derived from both singlet and triplet fluorenylidene.<sup>10</sup>

Irradiation of 36DAF in benzene gives primarily the addition product, norcaradiene 2, and a small amount of diazirine 1, eq 2. This behavior is essentially identical with



that observed for 18DAF. Photolysis of 36DAF in benzene containing  $\alpha$ -methylstyrene (1.0 M) gives norcaradiene 2 and cyclopropane 3 (4:1) and a small amount diazirine 1, eq 3. The ratio of cyclopropane to norcaradiene increases



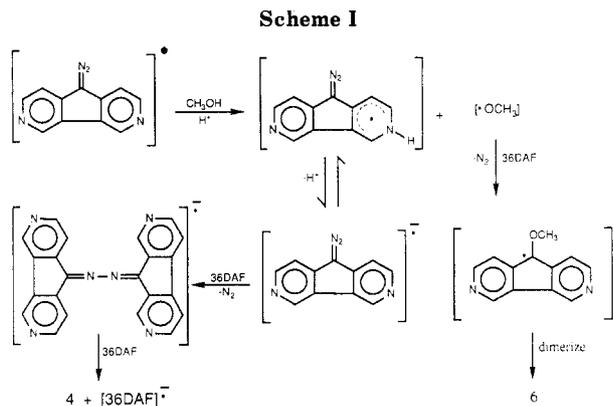
as the concentration of the  $\alpha$ -methylstyrene in the mixture is increased. For comparison, the yield of cyclopropane from photolysis of 36DAF is only slightly higher, at the same styrene concentration, than it is from the irradiation of 18DAF. In contrast, photolysis of DAF gives the expected cyclopropane in nearly quantitative yield at a lower  $\alpha$ -methylstyrene concentration, Table II.

The stereochemistry of cyclopropanation by 36FL was probed with (*E*)- $\beta$ -deuterio- $\alpha$ -methylstyrene. This olefin gives cyclopropanes in good yield from both singlet and triplet carbenes. Importantly, the Skell-Woodworth hypothesis has been verified for its reactions in every case examined. Irradiation of 36DAF in neat deuteriated  $\alpha$ -methylstyrene at 310 nm (into the  $\pi-\pi^*$  transition of the diazo compound) gives cyclopropane 3 in 75% yield. Under these conditions, 3 is formed with 94% retention of the olefin stereochemistry. When an identical sample is irradiated at 420 nm (into the  $n-\pi^*$  transition) only 63% retention is observed. Similar wavelength-dependent behavior was noted previously for the photochemistry of 18DAF. The data are summarized in Table II.

**5. Triplet-Sensitized Reaction of 36DAF with  $\alpha$ -Methylstyrene.** Irradiation of a benzene solution of 36DAF containing benzil at wavelengths greater than 380 nm (most of the light is absorbed by the sensitizer) gives primarily cyclopropane 3 and a small amount of norcaradiene 2 (from light unavoidably absorbed directly by

(10) Savino, T. G.; Senthilnathan, V. P.; Platz, M. S. *Tetrahedron* 1986, 42, 2167.





action mechanism involving odd-electron intermediates. It has recently been reported that the excited states of electron-deficient heterocyclic nitrogen compounds undergo seemingly endoergic single-electron-transfer reactions in alcoholic media.<sup>14</sup> This process is postulated to proceed via proton transfer from the alcohol to the excited heterocycle (in a presumed exciplex) with simultaneous electron transfer. Of course, the probability of operation of this pathway depends on the basicity of the compound. The increased basicity of 36DAF compared with 18DAF, revealed by their  $pK_b$  values, may trigger this reaction.

If the proton-electron transfer mechanism operates for irradiation of 36DAF in methyl alcohol, then it is a simple matter to account for our experimental observations by analogy with the electrochemical reduction of diazo compounds.<sup>12</sup> The proposed reaction sequence is outlined in Scheme I.

Irradiation of 36DAF in methyl alcohol creates an excited state capable of accepting a proton and an electron to form 36DAFH<sup>•+</sup> and a methoxy radical. We suspect that the short-lived intermediate with an absorption of 375 nm, detected in this reaction by UV and ESR spectroscopy, is 36DAFH<sup>•+</sup>. In the presence of base, this radical is deprotonated to form (36DAF)<sup>•-</sup>; the blue species also formed in the reduction of 36DAF by potassium. At a high initial 36DAF concentration, 36DAFH<sup>•+</sup> or (36DAF)<sup>•-</sup> combines with the ground state of the diazo compound to form (after loss of N<sub>2</sub>) the ketazine radical (or radical anion, depending on the pH). This intermediate continues the chain reaction, leading ultimately to ketazine 4. This postulate accounts for the concentration dependence of the quantum yield for consumption of 36DAF. Ether 6 is formed by addition of the methoxy radical to 36DAF and subsequent dimerization after the loss of N<sub>2</sub>.

### Conclusions

Except for strange behavior in methyl alcohol, the properties of 36DAF and 36FL resemble closely those for 18DAF and 18FL. This implicates a through-bond mechanism for the transmission of the electronic effect of the ring-nitrogen atoms. The irradiation of 36DAF in methyl alcohol appears to proceed by an unusual, but precedented, electron-transfer sequence to give odd-electron intermediates.

### Experimental Section

**General Procedures.** Routine <sup>1</sup>H NMR spectra were recorded on an XL-200 or QE-300 NMR spectrometer. Mass spectra were obtained with Varian MAT CH-5 and 731 mass spectrometers. Elemental analyses were performed by the Analysis Laboratory,

University of Illinois. UV-visible absorption spectra were recorded on a Perkin-Elmer 552 spectrophotometer. IR spectra were obtained from an IBM IR-32 instrument. Direct photolysis were carried out in a Rayonet photochemical reactor with 350-nm lamps or by irradiation with an Oriel mercury lamp equipped with suitable filters.

**Preparation of 36DAF.** 2,8-Phenanthroline, 3,6-diaza-9-fluorenone, and 36DAF were prepared according to literature procedures<sup>15</sup> for related compounds with some modifications.

**1. Preparation of 2,8-Phenanthroline.** A 3.0-g sample of *trans*-1,2-di-4-pyridylethylene was dissolved in 3.5 L of an acetonitrile/water (30:5) mixture. The solution was placed in an open container continuously purged with air and irradiated through quartz with a 450-W medium-pressure Hg lamp. The irradiation was complete in ca. 4 h. The solution was concentrated to ca. 500 mL, extracted with chloroform, and then crystallized from pentane to give white crystals of 2,8-phenanthroline (1.4 g).

**2. Preparation of 3,6-Diaza-9-fluorenone.** A 1.0-g sample of 2,8-phenanthroline was mixed with 1.5 g of potassium hydroxide and the resultant mixture then dissolved in water (150 mL). The solution was heated to boiling while a hot solution of potassium permanganate in water (2.5 g in 80 mL) was added over 10 min. After 5 min more at the boiling point, the hot reaction mixture was filtered and the yellow filtrate was cooled and extracted with chloroform. The solvent was removed from the extract leaving 3,6-diazafluorenone as yellow crystals. Recrystallization from acetone gave the following data: mp 167.5 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.66 (d, 2 H), δ 8.80 (d, 2 H), δ 9.05 (d, 2 H); MS (EI), *m/e* 182.0; exact MS calcd for C<sub>11</sub>H<sub>6</sub>N<sub>2</sub>O 182.0480, found 182.0482.

**3. Preparation of 9-Diazo-3,6-diazafluorene.** 3,6-Diaza-9-fluorenone (1.0 g) and *p*-toluenesulfonylhydrazide (2.0 g) were dissolved in 150 mL of ethyl alcohol, and the resultant mixture was kept at room temperature overnight. The yellow precipitate that formed was removed and redissolved in a mixture of 150 mL of chloroform and 150 mL of 2% aqueous KOH. The mixture was stirred at room temperature for 8 h, washed with fresh 2% KOH, and then extracted with chloroform. The combined organic solution was dried, the solvent removed under reduced pressure, and the residue chromatographed on silica gel with ethyl acetate/acetonitrile (1:1, v/v) to give a light yellow solid. Recrystallization from ethyl ether gave yellow crystals: mp 150 °C dec; MS (EI), *m/e* 194.0 (M<sup>+</sup>), 166; exact MS calcd for C<sub>11</sub>H<sub>6</sub>N<sub>4</sub> *m/e* 194.0594, found 194.0584; IR (CHCl<sub>3</sub>) 2077.6 cm<sup>-1</sup> (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.54 (dd, 2 H), δ 8.65 (dd, 2 H), δ 9.32 (d, 2 H).

**Direct Photolysis of 36DAF in Cyclohexane.** A 3.9 × 10<sup>-4</sup> M solution of 36DAF was placed in a quartz tube, purged with argon for 15 min, and then irradiated (Rayonet) until 95% of 36DAF had been consumed (determined by NMR spectral analysis). After filtration of a trace precipitate, the cyclohexane was removed under vacuum at room temperature. The solvent-insertion product was purified by chromatography on silica gel to give 7 in 85% yield: <sup>1</sup>H NMR δ 0.8–1.8 (m, 10 H), δ 2.20 (m, 1 H), δ 3.95 (d, 1 H), δ 7.50 (d, 2 H), δ 8.58 (d, 2 H), δ 9.10 (s, 2 H); MS (EI), *m/e* 250.0; exact MS calcd for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub> 250.1458, found 250.1464.

**Photolysis of 36DAF in Benzene.** A 2.1 × 10<sup>-3</sup> M solution of 36DAF in benzene was purged with Ar and then irradiated (Rayonet) for 10 min. <sup>1</sup>H NMR spectral analysis of the reaction mixture showed 2 (75.0%) and 1 (8.5%). The norcaradiene 2 was isolated by chromatography on silica gel. For 2: <sup>1</sup>H NMR δ 3.76 (m, 2 H), δ 6.22 (m, 2 H), δ 6.58 (m, 2 H), δ 7.02 (d, 2 H), δ 8.00 (d, 2 H), δ 9.12 (d, 2 H); exact mass calcd for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub> *m/e* 244.0984, found 244.0996. For 1: <sup>1</sup>H NMR δ 6.88 (d, 2 H), δ 8.62 (d, 2 H), δ 9.25 (d, 2 H); MS (EI), *m/e* 194.0; exact MS calcd for C<sub>11</sub>H<sub>6</sub>N<sub>4</sub> 194.0586, found 194.0589.

**Photolysis of 36DAF with  $\alpha$ -Methylstyrene (AMS) in Benzene.** A 4.38 × 10<sup>-3</sup> M solution of 36DAF in benzene containing 1.0 M AMS was purged with Ar and irradiated for 10 min (Rayonet). The <sup>1</sup>H NMR spectrum of the reaction mixture showed 2 (ca. 70%) and cyclopropane 3 (ca. 20%). Cyclopropane 3 was

(14) Caronna, T.; Morrocchi, S.; Vittimberga, B. M. *J. Am. Chem. Soc.* 1986, 108, 2205.

(15) (a) Perkampus, H. H.; Kassebeer, G. *Justus Liebigs Ann. Chem.* 1966, 696, 1. (b) Eckhard, I. F.; Summer, L. A. *Aust. J. Chem.* 1973, 26, 2727. (c) Yamamoto, Y.; Moritani, I. *Tetrahedron* 1970, 26, 1235. (d) Jonczyk, A.; Wostowska, J.; Makosza, M. *Bull. Soc. Chim. Belg.* 1977, 86, 739.

Table III. Irradiation of 36DAF in Methyl Alcohol

[36DAF], M	product yields (absolute), %			
	ketazine 4	diether 6	diazirine 1	ketone 5
$5.5 \times 10^{-3}$	75	2	20	2
$1.2 \times 10^{-3}$	40	20	10	10
$3.4 \times 10^{-4}$	2	30	10	50

isolated by chromatography on silica gel:  $^1\text{H NMR}$  for **3**  $\delta$  1.85 (s, 3 H),  $\delta$  2.30 (d, 1 H),  $\delta$  2.60 (d, 1 H),  $\delta$  5.75 (d, 1 H),  $\delta$  7.35 (d, 1 H),  $\delta$  8.05 (d, 1 H),  $\delta$  8.60 (d, 1 H),  $\delta$  9.05 (s, 1 H),  $\delta$  9.20 (s, 1 H); MS (EI),  $m/e$  284.0; exact MS calcd for  $\text{C}_{20}\text{H}_{16}\text{N}_2$  284.1317, found 284.1307.

**Triplet Sensitization of 36DAF with Benzil in Benzene and  $\alpha$ -Methylstyrene.** A benzene solution of 36DAF ( $1.03 \times 10^{-3}$  M) containing 1.0 M AMS and  $1.5 \times 10^{-2}$  M benzil was purged with Ar and irradiated (<380 nm). Analysis of the reaction by  $^1\text{H NMR}$  spectroscopy showed that the yield of cyclopropane **3** was more than 90%.

**Photolysis of 36DAF in Methyl Alcohol.** Several samples were prepared, each containing a different concentration of 36DAF ( $3.4 \times 10^{-4}$  to  $5.5 \times 10^{-3}$  M). All samples were purged with Ar and then irradiated (Rayonet). The amount of remaining 36DAF and the yields of the products were determined by  $^1\text{H NMR}$  spectroscopy. The results are summarized in Table III. Ketazine **4** and the dimethoxy ether **6** were isolated from the reaction mixture by chromatography on silica gel. For **6**:  $^1\text{H NMR}$   $\delta$  2.60

(s, 3 H),  $\delta$  6.90 (br, 2 H),  $\delta$  8.5 (m, 2 H),  $\delta$  8.84 (s, 2 H); MS (EI),  $m/e$  394.0; exact MS calcd for  $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_2$  394.1413, found 394.1421. For **3**:  $^1\text{H NMR}$   $\delta$  7.85 (d, 2 H),  $\delta$  8.00 (d, 2 H),  $\delta$  8.70 (d, 2 H),  $\delta$  8.85 (d, 2 H),  $\delta$  9.15 (s, 4 H); MS (EI),  $m/e$  360.0; exact MS calcd for  $\text{C}_{22}\text{H}_{12}\text{N}_4$  360.1115, found 360.1119.

**Reaction of 36DAF with Potassium.** A 15-mg sample of 36DAF was dissolved in 20 mL of dry,  $\text{N}_2$ -purged THF. A small piece of potassium (ca. 30 mg) was added to the solution; a blue color developed immediately. A 2.0-mL aliquot of the blue solution was transferred carefully under  $\text{N}_2$  to a  $\text{N}_2$ -purged solution of 36DAF in methyl alcohol (15 mg in 10 mL). After a few minutes, 4.5 mg (determined gravimetrically) of ketazine **4** precipitated from the alcohol solution. This corresponds to a ketazine yield of 300% based upon the maximum quantity of ketazine radical anion that could have been transferred to the methyl alcohol solution of 36DAF.

**Acknowledgment.** 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.** **2**, 109528-45-2; **3**, 109528-46-3; **4**, 109528-47-4; **6**, 109528-48-5; **7**, 109528-44-1; DAF, 832-80-4; 18DAF, 1807-47-2; 36DAF, 109528-41-8; FL, 2762-16-5; 18FL, 103621-90-5; 36FL, 109528-42-9; 2,8-phenanthroline, 230-46-6; 3,6-diaza-9-fluorene, 109528-43-0.

## A [1,2] and a [1,4] Shift in a Wittig Thioether Rearrangement. Isolation of a [1.1](2,8)Naphthalenophane Tautomer

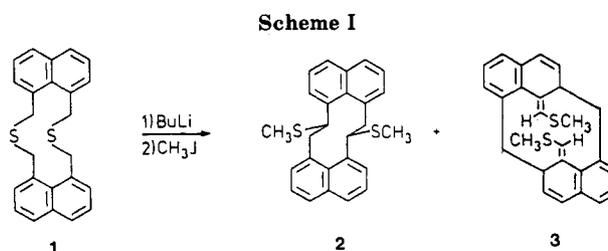
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Received February 27, 1987

Treatment of 7*H*,9*H*,16*H*,18*H*-dinaphtho[1,8-*cd*:1',8'-*ij*][1,7]dithiacyclododecin (**1**) with butyllithium and methyl iodide yields as the main product *anti*-7,8,15,16-tetrahydro-7,15-bis(methylthio)cyclodeca[1,2,3-*de*:6,7,8-*d'e'*]-dinaphthalene (**2**) and as a side product 1',2',7,8-tetrahydro-1',8-bis[(methylthio)methylene]-1,2':7,8'-dimethanodinaphthalene (**3**). The structures of both products have been elucidated by spectroscopic means as well as by X-ray investigations on crystals of **2** and **3**. The origin of **2** and **3** can be rationalized by assuming a [1,2] and a [1,4] shift, respectively, in a Wittig thioether rearrangement. Compound **3** represents the first [1.1](2,8)naphthalenophane tautomer.

The *S* analogue of the Wittig ether rearrangement<sup>1</sup> has been used recently to synthesize cyclophanes.<sup>2,3</sup> Usually [1,2] shifts are observed in this rearrangement;<sup>1-4</sup> in some cases, however, [1,4] shifts also occur.<sup>5</sup> In connection with our efforts to synthesize perpendicular  $\pi$ -systems separated by a four-membered ring,<sup>6</sup> we investigated a Wittig thioether rearrangement and observed a [1,4] shift.



The Wittig thioether rearrangement of 7*H*,9*H*,16*H*,18*H*-dinaphtho[1,8-*cd*:1',8'-*ij*][1,7]dithiacyclododecin (**1**), prepared according to Kemp et al.<sup>7</sup> has been investigated. The Wittig thioether rearrangement has been carried out according to a procedure described

(1) Schöllkopf, U. *Angew. Chem.* 1970, 82, 795; *Angew. Chem., Int. Ed. Engl.* 1970, 9, 763.

(2) Mitchell, R. H.; Otsubo, T.; Boekelheide, V. *Tetrahedron Lett.* 1975, 2193.

(3) Haenel, M. W.; Lintner, B.; Benn, R.; Rufinska, A.; Schroth, G., *Chem. Ber.* 1986, 118, 4922.

(4) Biellmann, J. F.; Schmitt, J. L. *Tetrahedron Lett.* 1973, 4615. Biellmann, J. F.; Ducep, J. B.; Schirlin, D. *Tetrahedron* 1980, 36, 1249.

(5) Felkin, H.; Tambute, A. *Tetrahedron Lett.* 1969, 821. Biellmann, J. F.; Ducep, J. B. *Ibid.* 1970, 2899; 1971, 33.

(6) Gleiter, R.; Schaaff, H. P.; Götzmann, W.; Rodewald, H.; Jahn, R.; Irgartinger, H. *Helv. Chim. Acta* 1987, 70, 480.

(7) Kemp, W.; Storie, I. T.; Tulloch, C. D. *J. Chem. Soc., Perkin Trans. 1* 1980, 2812.