Reactions of the Difluoromethylenimino Radical

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Abstract: The difluoromethylenimino radical, $CF_2{=}N\cdot$, has been generated by irradiation of tetrafluoro-2,3-diaza-1,3-butadiene, $CF_2{=}N{-}N{=}CF_2$, with ultraviolet light in quartz vessels. Conclusive spectroscopic evidence for the existence of the radical has not been obtained but it has been "trapped" by means of radical, carbene, and olefin coreactants. The ease with which the radical is generated and "trapped" suggests that $CF_2{=}N{-}N{=}CF_2$ may be a useful synthesis intermediate. The spectral properties of some perfluoro-α,ω-bisazomethines are reported.

A recent communication[1] has reported spectroscopic evidence for the transient existence of the methylenimino radical, $CH_2{=}N\cdot$, during the photolysis of 2,3-diaza-1,3-butadiene. Other workers have observed the electron spin resonance associated with this radical when HCN is photolyzed in the presence of HI.[2] The methylenimino radical is reported to decompose to

$$CH_2{=}N{-}N{=}CH_2 \xrightarrow{h\nu} 2CH_2{=}N\cdot \longrightarrow CH_2{=}NH + HC{\equiv}N$$

methylenimine and HCN,[1] thus rendering an investigation of its chemical properties very difficult.

We have reported[3,4] the synthesis of tetrafluoro-2,3-diaza-1,3-butadiene and have contrasted its thermal stability (stable at 200°)[4] with that of its hydrocarbon analog, which rapidly polymerizes at room temperature.[5]

The thermal stability of $CF_2{=}N{-}N{=}CF_2$, as well as the evidence for the formation of $CH_2{=}N\cdot$ from $CH_2{=}N{-}N{=}CH_2$, prompted us to investigate the possibility of generating the difluoromethylenimino radical, $CF_2{=}N\cdot$, by photolysis of $CF_2{=}N{-}N{=}CF_2$.[6]

Results and Discussion

The gas-phase far-ultraviolet spectrum of tetrafluoro-2,3-diaza-1,3-butadiene shows λ_{max} 180 mμ (ϵ 7434 l. mole^{-1} cm^{-1}) and photochemical studies required the use of quartz equipment. Electron spin resonance measurements at $-196°$ on the undiluted material or a 10% solution of the material in $CFCl_3$ indicated that there was a photoinduced signal in the $g = 2$ region but the fine structure of this signal was unobtainable under the conditions employed. Thus, it could not be assigned definitely to the $CF_2{=}N\cdot$ radical. Photolysis of $CF_2{=}N{-}N{=}CF_2$ in the presence of coreactants, however, did produce evidence for the formation of $CF_2{=}N\cdot$ and indicated that it was formed readily and could be employed as a synthesis intermediate and polymerization initiator. The difluoromethylenimino radical has been "trapped" by means of radical, carbene, and olefin coreactants.

Initial experiments to chemically "trap" the difluoromethylenimino radical involved the photolysis of an approximately stoichiometric mixture of tetrafluoro-2,3-diaza-1,3-butadiene and hexafluoroazomethane in the gas phase. Perfluoro-2-azapropene, $CF_2{=}N{-}CF_3$, was isolated in greater than a 10% yield (based on $CF_3{-}N{=}N{-}CF_3$) accompanied by larger amounts of hexafluoroethane. As expected, increasing the

$$CF_2{=}N{-}N{=}CF_2 \xrightarrow{h\nu} 2CF_2{=}N\cdot$$

$$CF_3{-}N{=}N{-}CF_3 \xrightarrow{h\nu} 2CF_3\cdot + N_2 \longrightarrow C_2F_6$$

$$CF_2{=}N\cdot + CF_3\cdot \longrightarrow CF_2{=}N{-}CF_3$$

ratio of $CF_2{=}N{-}N{=}CF_2$ to $CF_3{-}N{=}N{-}CF_3$ resulted in increased conversion of $CF_3{-}N{=}N{-}CF_3$ to $CF_3{-}N{=}CF_2$.

On the other hand, photolysis of $CF_2{=}N{-}N{=}CF_2$ in the absence of coreactants using a General Electric BH-6 lamp resulted in almost quantitative conversion to hexafluoro-2,4-diaza-1,4-pentadiene, $CF_2{=}N{-}CF_2{-}$

$$3CF_2{=}N{-}N{=}CF_2 \xrightarrow{h\nu} 2CF_2{=}N{-}CF_2{-}N{=}CF_2 + N_2$$

$N{=}CF_2$,[6] the first reported member of a series of perfluoro-α,ω-bisazomethines. This reaction is rationalized on the basis of decomposition of the azine into both $CF_2{=}N\cdot$ and difluorocarbene. Since no tetrafluoroethylene is produced it appears that the difluoromethylenimino radical is generated more readily than difluorocarbene, and radical combination reactions undoubtedly lead to the formation of the observed product.

The fact that $CF_2{=}N{-}CF_2{-}N{=}CF_2$ is produced in the above reaction indicates that the difluoromethylenimino radical, unlike the methylenimino radical, is intrinsically stable and does not readily decompose to $FC{\equiv}N$ and $CF_2{=}NF$. Such a decomposition would involve the transfer of a fluorine atom, which possesses relatively high mass, and the cleavage of a carbon–fluorine bond (bond strength ~111 kcal/mole).

In order to evaluate the ease with which $CF_2{=}N{-}N{=}CF_2$ could be used as a photochemical source of $CF_2{=}N\cdot$ and as such find utility as a synthesis technique, a number of additional reactions were carried out in which $CF_2{=}N{-}N{=}CF_2$ was photolyzed in the presence of difluorocarbene (simultaneously generated from difluorodiazirine) or olefin coreactants. In all cases, the ability of the difluoromethylenimino radical to enter into typical radical reactions was indicated.

Thus, the photolysis of a 2:1 mixture of tetrafluoro-2,3-diazabuta-1,3-diene and difluorodiazirine,[3,7] CF_2N_2, resulted in the formation of the first four members of the

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[1] J. F. Ogilvie, *Proc. Chem. Soc.*, 359 (1964).

[2] E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **36**, 1938 (1962).

[3] R. A. Mitsch, *J. Heterocyclic Chem.*, **1**, 59 (1964).

[4] R. A. Mitsch and P. H. Ogden, *J. Org. Chem.*, **31**, 3833 (1966).

[5] N. P. Neureiter, *J. Am. Chem. Soc.*, **81**, 2910 (1959).

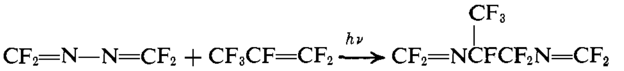
[6] R. A. Mitsch and P. H. Ogden, *Chem. Commun.*, 59 (1967).

[7] R. A. Mitsch, *J. Heterocyclic Chem.*, **1**, 233 (1964); **3**, 245 (1966).

perfluoro-α,ω-bisazomethines, $CF_2{=}N{-}(CF_2)_{1-4}{-}N{=}CF_2$, in isolable quantities. As discussed above, photolysis of $CF_2{=}N{-}N{=}CF_2$ in the absence of coreactants undoubtedly involves the generation of both $CF_2{=}N\cdot$ and $:CF_2$, but no tetrafluoroethylene. Thus, the role of CF_2N_2 is presumably to supply additional difluorocarbene, as well as C_2F_4, to the system. The formation of the perfluoro-α,ω-bisazomethines can then be rationalized as resulting from appropriate radical combinations and/or reaction with tetrafluoroethylene.

$$CF_2{=}N{-}N{=}CF_2 + CF_2N_2 \xrightarrow{h\nu} CF_2{=}N{-}(CF_2)_{1-4}{-}N{=}CF_2$$

In order to obtain further evidence for the above mechanism and to test the utility of $CF_2{=}N\cdot$ in preparative chemistry, additional perfluoro-α,ω-bisazomethines were prepared by photolysis of tetrafluoro-2,3-diaza-1,3-butadiene in the presence of various fluorinated olefins, as exemplified by the reaction with perfluoropropene shown below (see Table I).



$$CF_2{=}N{-}N{=}CF_2 + CF_3CF{=}CF_2 \xrightarrow{h\nu} CF_2{=}N\overset{\overset{\displaystyle CF_3}{|}}{C}FCF_2N{=}CF_2$$

Table I. α,ω-Bisazomethines

Coreactant	Product	% conversion[a]	T_r[b]
$CF_2:$[c,d]	$CF_2{=}N{-}CF_2{-}N{=}CF_2$	12	80
	$CF_2{=}N{-}(CF_2)_2{-}N{=}CF_2$	25	188
	$CF_2{=}N{-}(CF_2)_3{-}N{=}CF_2$	3	400
	$CF_2{=}N{-}(CF_2)_4{-}N{=}CF_2$	1	1200
$CF_2{=}CF_2$[d,e]	$CF_2{=}N{-}CF_2{-}N{=}CF_2$	13	
	$CF_2{=}N{-}(CF_2)_2{-}N{=}CF_2$	57	
	$CF_2{=}N{-}(CF_2)_3{-}N{=}CF_2$	10	
$CF_3{-}CF{=}CF_2$[f]	$CF_2{=}N{-}CF_2{-}N{=}CF_2$	11	
	$CF_2{=}N{-}CF(CF_3){-}CF_2{-}N{=}CF_2$	66	300
$CF_3{-}CF{=}CF{-}CF_3$[f]	$CF_2{=}N{-}CF_2{-}N{=}CF_2$	17	
	$CF_2{=}N{-}CF(CF_3){-}CF(CF_3){-}N{=}CF_2$	30	430
$CF_2{=}CFCl$[d,e]	$CF_2{=}N{-}CF_2{-}N{=}CF_2$	12	
	$CF_2{=}N{-}CF_2{-}CFCl{-}N{=}CF_2$	25	810

[a] Conversion based on $CF_2{=}N{-}N{=}CF_2$ consumed during the reaction. [b] T_r = relative retention time = $(T_{comp} - T_{air})/(T_{CFCl_3} - T_{air}) \times 100$. [c] CF_2: obtained *in situ* from CF_2N_2; a ratio of 2:1 CF_2N_2 to $CF_2{=}N{-}N{=}CF_2$ was employed. [d] Some telomeric material was also obtained. [e] The ratio of olefin to $CF_2{=}N{-}N{=}CF_2$ was 1:2. [f] The ratio of olefin to $CF_2{=}N{-}N{=}CF_2$ was 1:1.

The four olefins studied, tetrafluoroethylene, hexafluoropropene, octafluorobutene-2, and chlorotrifluoroethylene, all afforded the corresponding 1,2-bisazomethine as the major volatile product. As can be seen from Table I, in all cases a low yield of $CF_2{=}N{-}CF_2{-}N{=}CF_2$ was also obtained in the reactions with olefin coreactants. Although it is possible that this material arises through photolytic generation of difluorocarbene from the fluorinated olefins,[8] we were unable to definitely identify any material derived from carbenes such as $CFCl:$ or $CF_3CF:$. It is therefore concluded that the primary source of difluorocarbene leading to the formation of $CF_2{=}N{-}CF_2{-}N{=}CF_2$ is photolysis of tetrafluoro-2,3-diaza-1,3-butadiene.

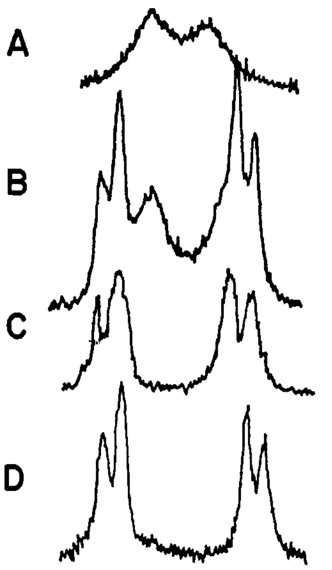


Figure 1. F^{19} nmr AB patterns: A, $CF_2{=}NCF(CF_3)CF(CF_3)N{=}CF_2$; B, $CF_2{=}NCF_2CF(CF_3)N{=}CF_2$; C, $CF_2{=}NCF_2CF_2N{=}CF_2$; and D, $CF_2{=}NCF_2CFClN{=}CF_2$.

The reactions were generally carried out by photolysis of a 1:1 or 2:1 gaseous mixture of $CF_2{=}N{-}N{=}CF_2$ and olefin in a quartz bulb. The perhalo-α,ω-bisazomethines prepared in this manner are colorless, volatile liquids which can be separated from the starting materials and reaction by-products by fractional distillation–condensation and/or by gas–liquid partition chromatography. However, they are quite sensitive to the presence of moisture and undergo rapid hydrolysis.

They were identified primarily by infrared, F^{19} nuclear magnetic resonance, and mass spectroscopy (see Table II) and in some cases by elemental analyses. The $CF_2{=}N{-}$ group of the α,ω-bisazomethines exhibits an absorption in the 5.44–5.62-μ region in the infrared and appears as an AB type pattern in the F^{19} nmr spectra.

The broadening of the F^{19} nmr AB pattern of the terminal $CF_2{=}N{-}$ moiety when adjacent to a $-CF(CF_3)-$ group is of some interest (Figure 1). This effect, which has not been observed previously in azomethines, and is probably caused by rapid stereoisomerization about the $C{=}N$ bond, is currently being investigated.

Experimental Section

Infrared spectra were measured on either a Perkin-Elmer Model 21 or 521 double-beam instrument using a 2.5-cm gas cell fitted with NaCl windows. Ultraviolet spectra were obtained on a Beckman DK-2A far-ultraviolet spectrophotometer using 5.0-cm gas cells. Electron spin resonance measurements were made using a Varian V-4502 instrument operating at 9500 Mc and a Pen-Ray low-pressure quartz Model 11 SC-1C ultraviolet source. Nuclear magnetic resonance measurements were made with a Varian V-4300-2 instrument operating at 40.0 Mc and utilizing an internal standard of $CFCl_3$ for the determination of chemical shifts. The values reported are ϕ^* [9] values at a dilution of 10–25%. Trifluoroacetic acid is ϕ^* 76.5 on this scale. Mass spectra were mea-

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[8] See E. Atkinson, *J. Chem. Soc.*, 2684 (1952); S. V. R. Mastrangelo, U. S. Patent 2,338,864 (1966); and J. Heicklen and V. Knight, *J. Phys. Chem.*, 64, 3600 (1965), for discussions pertaining to the photolytic generation of fluorocarbenes from olefins.

[9] G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, 63, 761 (1959).

Table II. F^{19} Nmr and Infrared Spectra

	F^{19} nmr			Infrared
Azomethines	ϕ^{*9}	Group	J_{AB}, cps	>C=N—, μ
$CF_3N{=}CF_2$	30.1 50.1	$CF_2{=}N$	82.0[e]	5.53 (s)
	56.5	CF_3		
$CF_2{=}N{-}N{=}CF_2$	51.7 73.5	$CF_2{=}N$	65	5.61 (m) 5.75 (s)
$CF_2{=}N{-}CF_2{-}N{=}CF_2$	32.0 50.9	$CF_2{=}N$	82.0	5.53 (m)[d] 5.61 (s)
	60.4[a]	CF_2		
$CF_2{=}N{-}(CF_2)_2{-}N{=}CF_2$	29.4 45.9	$CF_2{=}N$	83.0	5.62 (s)
	97.3[a]	CF_2CF_2		
$CF_2{=}N{-}CF_2CF(CF_3)\,N{=}CF_2$ (1) (2)	30.0 45.3	$CF_2{=}N$ (1)	81.0	5.49 (s)[d]
	34.6 42.8	$CF_2{=}N$ (2)	Broad	5.55 (s)
	79.1[b]	CF_3		
	91.3[a]	CF_2		
	153.8[a]	CF		
$CF_2{=}NCF(CF_3)CF(CF_3)N{=}CF_2$	35.2 41.6	$CF_2{=}N$	Broad	5.49 (s)[d] 5.52 (s)
	78.2[c]	CF_3		
	149.5[a]	CF		
$CF_2{=}N{-}CF_2CFCl{-}N{=}CF_2$	30.1 46-1	$CF_2{=}N$	84.0	5.53 (m)[d]
	94.7[a]	CF_2		5.58 (s)
	95.9[a]	CFCl		

[a] Peak was broad and its fine structure unobtainable. [b] Triple (J = 10.6 cps) doublet (very small). [c] Doublet (J = 7.5 cps). [d] Shoulder. [e] N. Muller, P. C. Lauterbur, and S. F. Svatos, *J. Am. Chem. Soc.*, 79, 1807 (1957).

sured utilizing a Consolidated 21-103C instrument with an inlet temperature of 30°, ion chamber temperature of 250°, ion voltage of 70 v, and ion current of 10 μa. The most significant peaks are reported and are expressed as: *m/e* (relative intensity) proposed ion. Molecular weights were determined from effusion measurements. Vapor phase chromatographic separations were achieved with either a 2 m × 0.5 in. or 0.5 m × 0.5 in. KEL-F 8126 column, and by condensing products from the effluent gas at −196° in a trap filled with glass beads. Ultraviolet light was obtained either from a 1000-w General Electric BH-6, a Hanovia 140-, or a Hanovia 450-w lamp.

Photolysis with Hexafluoroazomethane. Tetrafluoro-2,3-diaza-1,3-butadiene, $CF_2{=}N{-}N{=}CF_2$ (0.05 g, 0.39 mmole), and hexafluoroazomethane, $CF_3{-}N{=}N{-}CF_3$ (0.06 g, 0.4 mmole), were condensed into a silica tube fitted with a Fischer-Porter polytetrafluoroethylene valve, at −196°, and photolyzed for 16 hr at room temperature using a Hanovia 140-w lamp. Pentafluoro-3-azapropene, $CF_3{-}N{=}CF_2$ (0.04 mmole, 10%), was isolated from the product by vapor phase chromatography and identified by comparison of its infrared spectrum with that of an authentic sample. The majority of the $CF_2{=}N{-}N{=}CF_2$ was recovered unchanged.

Photolysis with Difluorodiazirine. Tetrafluoro-2,3-diaza-1,3-butadiene (0.57 g, 4.5 mmoles) and difluorodiazirine, CF_2N_2 (0.67 g, 8.6 mmoles), were condensed under vacuum into a silica tube fitted with a Fischer-Porter polytetrafluoroethylene valve and photolyzed for 4 hr at room temperature using a General Electric BH-6 lamp. Hexafluoro-2,4-diaza-1,4-pentadiene, $CF_2{=}N{-}CF_2{-}N{=}CF_2$ [0.56 mmole, 12.5% (*Anal.* Calcd for $C_3F_6N_2$: F, 63.0; mol wt, 178. Found: F, 63.4; mol wt, 179)], octafluoro-2,5-diaza-1,5-hexadiene, $CF_2{=}N{-}(CF_2)_2{-}N{=}CF_2$ [1.14 mmoles, 25% (*Anal.* Calcd for $C_4F_8N_2$: F, 66.5; mol wt, 228. Found: F, 67.6; mol wt, 226)], decafluoro-2,6-diaza-1,6-heptadiene, $CF_2{=}N(CF_2)_3{-}N{=}CF_2$ (0.012 mmole, 2.5%, >C=N— absorption 5.55 μ), and dodecafluoro-2,7-diaza-1,7-octadiene, $CF_2{=}N(CF_2)_4{-}N{=}CF_2$ (0.005 mmole, 1.5%, >C=N— absorption 5.55 μ) were isolated by fractional distillation–condensation followed by vapor phase chromatography and characterized by their infrared and mass spectra.

The mass spectra of $CF_2{=}N{-}CF_2{-}N{=}CF_2$ and $CF_2{=}N{-}CF_2{-}CF_2{-}N{=}CF_2$ are summarized as follows: $CF_2{=}N{-}CF_2{-}N{=}CF_2$: 26 (1.7) CN, 28 (1.8) N_2, 31 (28.1) CF, 45 (13.1) CFN, 41.5 (47.5) CF_3N^{2+}, 50 (30.9) CF_2, 64 (4.4) CF_2N, 69 (100) CF_3, 70 (5.0) $C_3F_4N_2^{2+}$, 71 (2.1) C_2FN_2, 76 (2.4) C_2F_2N, 90 (2.2) $C_2F_2N_2$, 95 (5.4) C_2F_3N, 114 (99.0) C_2F_4N, 139 (7.6) $C_3F_5N_2$, and 178 (1.8) $C_3F_6N_2$; $CF_2{=}N{-}CF_2CF_2{-}N{=}CF_2$: 14 (1.1) N, 28 (6.6) N_2, 31 (22.1) CF, 45 (1.4) CFN, 50 (24.9) CF_2, 64 (1.2) CF_2N, 69 (89.1) CF_3, 70 (3.0) $C_3F_4N_2^{2+}$, 71 (1.3) C_2FN_2, 76 (2.9) C_2F_2N, 90 (1.3) $C_2F_2N_2$, 95 (5.5) C_2F_3N, 114 (100) C_2F_4N, 121 (1.1) $C_3F_3N_6$, 159 (6.0) $C_3F_5N_2$, and 178 (1.1) $C_3F_6N_2$.

Photolysis with Tetrafluoroethylene. a. Using Excess $CF_2{=}N{-}N{=}CF_2$. Tetrafluoro-2,3-diaza-1,3-butadiene (0.15 g, 1.17 mmoles) and tetrafluoroethylene (0.056 g, 0.56 mmole) were condensed under vacuum into a silica tube fitted with a Fischer-Porter polytetrafluoroethylene valve and photolyzed for 80 hr at room temperature using a Hanovia 140-w lamp. Tetrafluoro-2,3-diaza-1,3-butadiene (0.14 mmole, 12%), hexafluoro-2,4-diaza-1,4-pentadiene (0.13 mmole, 12.6%), octafluoro-2,5-diaza-1,5-hexadiene (0.585 mmole, 57%), and decafluoro-2,6-diaza-1,5-heptadiene were isolated by fractional distillation–condensation followed by vapor phase chromatography and were identified by their infrared and mass spectra.

b. Using Excess $CF_2{=}CF_2$. Tetrafluoro-2,3-diaza-1,3-butadiene (one part by gas volume) and tetrafluoroethylene (ten parts by gas volume) were condensed under vacuum into a silica tube which was fitted with a Fischer-Porter polytetrafluoroethylene valve and comprised of two separable halves, and photolyzed for 5 hr at room temperature using a General Electric BH-6 lamp. A white solid was produced which was shown by its infrared spectrum to be $CF_2{=}N(CF_2)_n{-}N{=}CF_2$, together with a trace of octafluoro-2,5-diaza-1,5-hexadiene, which was identified by its infrared spectrum.

Photolysis with Hexafluoropropene. Tetrafluoro-2,3-diaza-1,3-butadiene (0.15 g, 1.17 mmoles) and hexafluoropropene (0.174 g, 1.16 mmoles) were condensed under vacuum into a silica tube fitted with a Fischer-Porter polytetrafluoroethylene valve and photolyzed for 24 hr at room temperature using a General Electric BH-6 lamp. Tetrafluoro-2,3-diaza-1,3-butadiene (0.095 mmole, 8%), hexafluoro-2,4-diaza-1,4-pentadiene (0.117 mmole, 11%), and decafluoro-3-methyl-2,5-diaza-1,5-hexadiene, $CF_2{=}N{-}CF_2{-}CF(CF_3){-}N{=}CF_2$ [0.7 mmole, 66% (*Anal.* Calcd for $C_5F_{10}N_2$: F, 68.3; N, 10.1; mol wt, 278. Found: F, 66.9; N, 9.7; mol wt, 290)], were isolated by fractional distillation–condensation followed by vapor phase chromatography and identified by their infrared spectra. The mass and F^{19} nmr spectra of $CF_2{=}N{-}CF_2{-}CF(CF_3){-}N{=}CF_2$ were also obtained. Some higher molecular weight material was also isolated but was not characterized further.

The mass spectrum of $CF_2{=}N{-}CF_2{-}CF(CF_3){-}N{=}CF_2$ is summarized as follows: 28 (3.1) N_2, 31 (14.1) CF, 50 (15.1) CF_2, 69 (65.1) CF_3, 76 (6.4) C_2F_2N, 95 (6.3) C_2F_3N, 100 (1.4) C_2F_4, 114 (100)

C_2F_4N, 121 (1.3) $C_3F_3N_2$, 145 (1.6) C_3F_5N, 164 (17.8) C_3F_6N, 171 (1.3) $C_4F_5N_2$, 209 (3.0) $C_4F_7N_2$, and 214 (1.5) C_4F_8N.

Photolysis with Octafluorobutene-2. Tetrafluoro-2,3-diaza-1,3-butadiene (0.15 g, 1.17 mmoles) and octafluorobutene-2 (0.234 g, 1.17 mmoles) were condensed under vacuum into a silica tube fitted with a Fischer-Porter polytetrafluoroethylene valve and photolyzed for 12 hr at room temperature using the BH-6 lamp. Octafluorobutene-2 (0.58 mmole, 50%), hexafluoro-2,4-diaza-1,4-pentadiene (0.2 mmole, 15%), and dodecafluoro-3,4-dimethyl-2,5-diaza-1,5-hexadiene, $CF_2{=}N{-}CF(CF_3){-}CF(CF_3){-}N{=}CF_2$ [0.35 mmole, 30% (*Anal.* Calcd for $C_6F_{12}N_2$: F, 69.5; mol wt, 328. Found: F, 67.6; mol wt, 324)], were isolated by fractional distillation-condensation and vapor phase chromatography. The mass spectrum of $CF_2{=}N{-}CF(CF_3){-}CF(CF_3){-}N{=}CF_2$ is summarized as follows: 31 (17.4) CF, 50 (16.8) CF_2, 69 (100) CF_3, 76 (10.6) C_2F_2N, 95 (9.3) C_2F_3N, 100 (2.1) C_2F_4, 114 (75) C_2F_4N, 121 (2.4) $C_3F_3N_2$, 126 (2.8) C_3F_4N, 145 (3.1) C_3F_5N, 164 (85.2) C_3F_6N, 176 (1.4) C_4F_6N, 190 (1.0) $C_4F_6N_2$, 221 (2.6) $C_5F_7N_2$, and 259 (1.7) $C_5F_9N_2$.

Photolysis with Chlorotrifluoroethylene. Tetrafluoro-2,3-diaza-1,3-butadiene (0.26 g, 2.0 mmoles) and chlorotrifluoroethylene (0.15 g, 1.0 mmole) were condensed under vacuuum into a 5-l. flask fitted with a water-cooled quartz insert and irradiated for 35 min with a Hanovia 450-w, low-pressure ultraviolet light.

Hexafluoro-2,4-diaza-1,4-pentadiene (0.12 mmole, 12%) and heptafluoro-2,5-diaza-3-chloro-1,5-hexadiene (0.23 mmole, 23%) were isolated from the crude products by vapor phase chromatography and characterized by their infrared, mass, and F^{19} nmr spectra.

The mass spectrum of $CF_2{=}N{-}CF_2{-}CFCl{-}N{=}CF_2$ is summarized as follows: 31 (33.1) CF, 35 (2.5) Cl, 45 (1.4) CFN, 50 (35.6) CF_2, 57 (1.2) C_2FN, 66 (1.7) CFCl, 69 (100) CF_3, 76 (21.1) C_2F_2N, 81 (1.0) C_2F_2, 85 (17.7) CF_2Cl, 92 (1.2) C_2FClN, 95 (17.4) C_2F_3N, 111 (1.1) C_2F_2ClN, 114 (83.4) C_2F_4N, 121 (5.2) $C_3F_3N_2$, 130 (60.2) C_2F_3ClN, 145 (3.1) C_3F_5N, 159 (3.1) $C_3F_5N_2$, 180 (2.4) C_3F_5ClN, and 209 (14.4) $C_4F_7N_2$.

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Reaction of Chlorophylls a and b with Amines. Isocyclic Ring Rupture and Formation of Substituted Chlorin-6-amides[1]

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Abstract: Spectral studies of the reaction of amines with chlorophylls a and b confirm the fact that, with primary and secondary amines, cleavage of ring V occurs. With chlorophyll b reaction also occurs at the formyl group when primary amines are used. Kinetic data indicate that alcohol and water have a marked effect on the rate of the reaction in pure amines. Chemical and chromatographic studies support the spectral observations.

The β-keto ester system in ring V of chlorophylls a and b (**1a**) and related compounds is particularly sensitive to nucleophilic attack by alkoxides and by amines.[3] Nomenclature and proton numberings are shown in Figures 1 and 2. Ring V has frequently been the focus of attention because of the special role it may play in photosynthesis. It is the site of oxidation reactions leading to 10-hydroxy derivatives by enzymatic reactions[4a] and by the allomerization reaction.[4b] The keto group in ring V coordinates with magnesium to give chlorophyll aggregates in nonpolar solvents.[5] This group is also the site of attack by amines.

Fischer and co-workers[6] investigated the reactions of magnesium-free derivatives of chlorophyll such as methyl pheophorbide, *meso*-pheophorbide, and methyl pheoporphyrin with bases such as ammonia, piperidine, methylamine, hydrazine, and phenylhydrazine. Fischer concluded that ring V was cleaved and that chlorin-6-amide derivatives were formed.

Weller and Livingston[3b] extended Fischer's work to include chlorophylls a and b. On the basis of analogy they proposed that ring V was cleaved and that a substituted chlorin-6-amide was formed, apparently with retention of the magnesium. With chlorophyll b (**1b**) it was not clear from their data whether or not reaction also occurred at the formyl group. The spectral data also made it difficult to be certain of ring V

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