0.40 g (4 mmoles) of chromium(VI) oxide in 30 ml of glacial acetic acid and 1 ml of water. The mixture was heated at 90–100° for 3 hr and then poured into 200 ml of ice-water. This mixture was continuously extracted with ether for 5 days and the resulting organic layer dried over sodium sulfate. Removal of the solvents and chromatography of the residue on 35 g of silica gel afforded 0.23 g (85%) of *p*-nitrobenzoic acid (80–100% chloroform–benzene as eluent) which was crystallized from water to give yellow leaflets, mp 240–240.5° (lit.[54] mp 238°), and 0.10 g (77%) of phthalic acid (acetone–chloroform as eluent), mp 191° dec, which was identical with the material previously obtained (*vide supra*). Also obtained were 0.03 g of unreacted starting material and *ca.* 0.02 g of a ketone-containing product (infrared) which could not be purified.

B. Compound XXVIa. An oxidation similar to that in A resulted in the formation of 0.14 g (52%) of *p*-nitrobenzoic acid and 0.06 g (46%) of phthalic acid as well as some of the starting material XXVIa.

Isomerization of the *cis,trans*-Bisbenzylidene Compounds. A. The Olefin XXVIa. A solution of 0.11 g (0.3 mmole) of the olefin XXVIa and 0.17 g (0.6 mmole) of XI in 40 ml of anhydrous DMF was stirred under nitrogen for 48 hr at room temperature. When the solution was poured into 150 ml of ice-water, a yellow precipitate formed, which, when filtered and crystallized from benzene-carbon tetrachloride, gave 0.075 g (68%) of the *cis,cis* isomer XXVa, mp 282–284°, identical with an authentic sample by infrared comparison. The benzene–carbon tetrachloride solution was evaporated to dryness and *ca.* 0.03 g of the slightly impure starting material XXVIa was obtained. By extracting the water solution with ether, 0.14 g (82.4%) of the oxide XI was obtained.

A similar, though less facile, isomerization could be accomplished in boiling solvents such as acetone, benzene, and chloroform.

B. The Olefin XXVIc. A solution of 0.11 g (0.25 mmole) of the *cis,trans* isomer XXVIc and 0.14 g (0.5 mmole) of the compound XI in 15 ml of anhydrous DMF was treated as in A. The ice-water slurry was extracted with ether (three 100-ml portions), and the combined ether solutions were dried over sodium sulfate. The ether was evaporated, and the semisolid mixture obtained was chromatographed on a 1 × 50 cm column containing 20 g of Alcoa No. 71707 alumina to afford 0.066 g (60%) of the unisomerized *cis,trans* isomer XXVIc, 0.015 g (13.6%) of the isomerized *cis,cis* isomer XXVc, and 0.13 g of the oxide XI.

Dipole Moments of *cis,cis*- and *cis,trans*-Bisbenzylidene Compounds XXVc and XXVIc.[55] Dielectric constant measurements of the compounds XXVc and XXVIc in solvent carbon tetrachloride at 25 ± 0.01° provide the data necessary to obtain dipole moments calculated by the method of Halverstadt and Kumler.[56] The terms P_{E_2} and P_{A_1} are calculated by the methods reported in the literature (ref 57 and 58, respectively). According to the above, for XXVc and XXVIc, μ = 0.69 ± 0.18 and 2.301 ± 0.017 D., respectively. The less precise index of refraction method[59,60] gives, correspondingly, μ = 0.70 ± 0.30 and 2.21 ± 0.12 D.

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[54] Reference 46, p 100.

[55] We sincerely thank Professor C. F. Wilcox, Jr. for his help in obtaining the dipole moments.

[56] I. F. Halverstadt and W. K. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

[57] R. J. W. Le Fèvre and K. D. Steel, *Chem. Ind.* (London), 670 (1961).

[58] A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., p 582.

[59] E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).

[60] J. W. Smith, *ibid.*, **46**, 394 (1950), and references therein.

The Isomerization of Perfluoro-α,ω-bisazomethines

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Contribution No. 438 from the Central Research Laboratories, Minnesota Mining and Manufacturing Company, St. Paul, Minnesota 55119. *Received April 26, 1967*

Abstract: Perfluoro-α,ω-bisazomethines isomerize readily in the presence of fluoride ions to produce the corresponding terminal trifluoromethylbisazomethines. In general, an S$_{N}$2′ mechanism is thought to be operative in these isomerizations; however, the results indicate that, in some cases, this may not be true. The geometrical isomerization of some of the materials is discussed in terms of the F^{19} nuclear magnetic resonance spectral data. The spectral properties of several novel perfluorobisazomethines are reported.

We[1] have recently reported the preparation of several perfluoro-α,ω-bisazomethines from the photolysis of tetrafluoro-2,3-diazabuta-1,3-diene in the presence of fluoroolefin or fluorocarbene coreactants.

Fluoroolefins containing terminal double bonds have been shown to isomerize in the presence of fluoride ion.[2] No such isomerization has yet been reported for perfluoroazomethines, although the terminal $CF_2{=}N$ group is susceptible to attack by fluoride ion as indicated by the dimerization of perfluoro-2-azapropene, $CF_3N{=}CF_2$.[3]

Results and Discussion

Perfluoro-2,4-diazapenta-1,4-diene (I) and perfluoro-2,5-diazahexa-1,5-dienes[1] have been found to isomerize readily in the presence of fluoride ions to the corresponding bis(trifluoromethyl)carbodiimide (II) and 2,5-diazahexa-2,4-dienes, respectively. In general, treatment of a perfluoro-α,ω-bisazomethine with cesium

$$\underset{\text{I}}{CF_2{=}NCF_2N{=}CF_2} \xrightarrow{F^-} \underset{\text{II}}{CF_3N{=}C{=}NCF_3}$$

$$CF_2{=}NCFXCFXN{=}CF_2 \xrightarrow{F^-} CF_3N{=}CXCX{=}NCF_3$$

$$X = F, CF_3$$

fluoride causes complete isomerization; however, partially isomerized material or starting material was obtained in some cases. The boiling points of the isomerized bisazomethines were generally observed (see Table I) to be lower than those of the α,ω-bisazomethine starting materials. This observation is consistent with the boiling point differences noted by Miller[2] for terminal and internal perfluorodienes.

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[1] P. H. Ogden and R. A. Mitsch, *J. Am. Chem. Soc.*, **89**, 3868 (1967).

[2] W. T. Miller, W. Frass, and P. R. Resnick, *ibid.*, **83**, 1767 (1961).

[3] R. E. Banks, "Fluorocarbons and Their Derivatives," Oldbourne Press, London, 1964.

Table I. Properties of Bisazomethines

Compound	No.	T_r^{a}	Bp,^{b} °C	>C=N—, μ
$CF_2{=}NCF_2N{=}CF_2$	I	80	43	5.53 (m), 5.61(s)
$CF_3N{=}C{=}NCF_3$	II	21	7	4.52^c(s)
$CF_2{=}NCF_2CF_2N{=}CF_2$	III	188	62	5.62(s)
$CF_3N{=}CFCF{=}NCF_3$	IV	200	58	5.72(s)
$CF_2{=}NCF_2CF(CF_3)N{=}CF_2$	V	300	75	5.49(s),^{d} 5.55(s)
$CF_3N{=}CFCF(CF_3)N{=}CF_2$	VI	...	...	5.55(s), 5.61(s)
$CF_3N{=}CFC(CF_3){=}NCF_3$	VII	75	29	5.65(s), 5.83(s)
$CF_2{=}NCF(CF_3)CF(CF_3)N{=}CF_2$	VIII	430	113	5.49(s),^{d} 5.52(s)
$CF_3N{=}C(CF_3)C(CF_3){=}NCF_3$	IX	100	*e*	5.78(s), 5.85(s)
$CF_3NCF(CF_3)C(CF_3){=}NCF_2$	X	230	*e*	Not observed
$CF_2{=}NCF_2CFClN{=}CF_2$	XI	810	...	5.53(m),^{d} 5.58(s)
$CF_3N{=}CFCF{=}NCF_2Cl$	XII	...	...	5.75(s)

[a] T_r = relative retention time = $100(T_{compd} - T_{air})/(T_{CFCl_3} - T_{air})$. [b] Bp = boiling point determined by isoteniscope. [c] Absorption due to N=C=N stretching. [d] Shoulder. [e] The boiling point of a 2:1 mixture of IX and X was 69° (approx).

Table II. F^{19} Nmr Spectra

Compound	Group	ϕ*^{d}	Coupling, cps^a
$CF_3N{=}C{=}NCF_3$ (II)	CF_3	50.2	
$CF_3N{=}CFCF{=}NCF_3$ (IV)	CF_3	57.7	d, 14.2
	CF	25.0	q, 14.2
(1) (2) $CF_3N{=}CFCF(CF_3)N{=}CF_2$ (VIa) (*trans* isomer)	CF_2	44.0 30.8	AB^b
	$CF_3(2)$	81.3	
	CF	143.9	
	=CF	23.2	
	$CF_3(1)$	57.4	d, 13.3
(1) (2) $CF_3N{=}CFCF(CF_3)N{=}CF_2$ (VIb) M	CF_2^{c}		
	$CF_3(2)$	79.0	
	CF	131.6	
	=CF	17.6	
	$CF_3(1)$	54.2	d, <6
(1) (2) (3) $CF_3N{=}CFC(CF_3){=}NCF_3$ (VIIa)	$CF_3(1)$	57.3	d, 14.3
	$CF_3(2)$	70.7	d, very small
	$CF_3(3)$	60.9	d, 7.7
	CF	4.5	c
(1) (2) (3) $CF_3N{=}CFC(CF_3){=}NCF_3$ (VIIb)	$CF_3(1)$	56.8	f, 6.0
	$CF_3(2)$	70.2	c
	$CF_3(3)$	62.1	c
	CF	20.1	c
(1) (2) $CF_3N{=}C(CF_3)C(CF_3){=}NCF_3$ (IX)	$CF_3(1)$	60.9	c
	$CF_3(2)$	69.3	c
(1) (2) (3) $CF_3NCF(CF_3)C(CF_3){=}NCF_2$ (X)	$CF_3(1)$	54.9	c
	$CF_3(2)$	77.2	c
	$CF_3(3)$	68.0	c
	CF_2	66.1 70.7	AB, 166
	CF	136.1	c
$CF_3N{=}CFCF{=}NCF_2Cl$ (XII)	CF_3	57.6	d, 14.1
	CF_2Cl	36.5	d, 15.6
	CF	27.0	c
	CF	25.6	c

[a] d, doublet; t, triplet; q, quadruplet; f, fivefold; c, complex. [b] The presence of a CF_3 group adjacent to the $N{=}CF_2$ moiety has been shown to broaden the AB pattern and *J* values are unobtainable: P. H. Ogden and G. V. D. Tiers, *Chem. Commun.*, 527 (1967). [c] Broad AB pattern was unresolved from the *trans* isomer. [d] See ref 8.

Bis(trifluoromethyl)carbodiimide. In the presence of cesium fluoride, perfluoro-2,4-diazapenta-1,4-diene (I) isomerizes rapidly at room temperature to bis(trifluoromethyl)carbodiimide,[4] $CF_3N{=}C{=}NCF_3$ (II). Bis(trifluoromethyl)carbodiimide is the first reported member of a new class of compounds, the perfluoroalkylcarbodiimides, and was identified by its elemental analysis and infrared, mass, and F^{19} nmr spectra. It is a colorless, volatile liquid (bp 7°) which exhibits a strong absorption at 4.52 μ assigned to the N=C=N stretching frequency in its infrared spectrum. Other spectral properties and the elemental analysis of bis(trifluoromethyl)carbodiimide are reported in Tables I–IV.

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

Table III. Mass Spectra of I–IV, XI, and XII

m/e	Assigned ion	Pattern % I	II	III	IV	XI	XII
26	CN	1.7	1.0	...	...	...	...
28	N_2	1.8	1.6	1.0	6.6	...	...
31	CF	28.1	9.8	11.0	22.1	33.1	25.5
35	Cl	...	...	...	...	2.5	3.8
45	CFN	13.1	1.0	...	1.4	1.4	...
47	CCl	...	...	...	...	...	3.2
47.5	$C_2F_3N^{2+}$	47.5	...	...	...	...	...
50	CF_2	30.9	6.0	8.2	24.9	35.6	16.9
57	C_2FN	...	...	...	...	1.2	1.3
64	CF_2N	4.4	...	...	1.2	1.1	...
66	CFCl	...	...	...	...	1.7	2.1
69	CF_3	100	100	100	89.1	100	100
70	$C_3F_4N_2^+$	6.2	...	...	3.9	...	...
71	C_2FN_2	2.1	1.9	...	1.3	...	...
76	C_2F_2N	2.4	1.0	2.0	2.9	12.1	6.3
81	C_2F_3	...	...	...	...	1.0	...
83	CF_3N	...	...	...	...	...	2.1
85	CF_2Cl	...	...	...	...	17.7	43.2
90	$C_2F_2N_2$	2.2	2.6	...	1.3	...	...
92	C_2FNCl	...	...	...	...	1.2	3.2
95	C_2F_3N	5.4	...	7.1	5.5	17.4	12.7
100	C_2F_4	...	1.2	...	...	...	...
111	C_2F_2NCl	...	...	...	...	1.1	1.6
114	C_2F_4N	99.0	1.4	21.7	100	83.4	16.7
121	$C_3F_3N_2$	...	...	2.6	1.1	5.2	4.9
130	C_2F_3NCl	...	...	...	...	60.2	12.4
131	C_3F_5	...	...	...	...	...	7.0
140	$C_3F_4N_2$	...	...	1.5	...	...	...
145	C_3F_5N	...	...	...	...	3.1	...
159	$C_3F_5N_2$	7.6	12.9	1.3	6.0	3.1	1.3
178	$C_3F_6N_2$	1.8	11.8	...	...	...	...
180	C_3F_5NCl			...	...	2.4	...
183	C_3F_7N			1.8	...	...	...
190	$C_3F_6N_2$			...	1.1	...	...
209	$C_4F_7N_2$			1.0	...	14.4	22.3
228	$C_4F_8N_2$			2.3	...	...	...
Molecular weights		179	179	226	231	245	NA

Table IV. Elemental Analyses

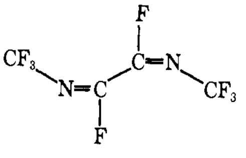
Compound	Calcd, % F	N	Found, % F	N
$CF_3N{=}C{=}NCF_3$ (II)	64.0	15.7	63.5	16.0
$CF_3N{=}CFCF{=}NCF_3$ (IV)	66.6	12.3	66.8	12.4
$CF_3N{=}CFC(CF_2){=}NCF_3$ (VII)	68.3	10.1	68.6	10.0
$CF_3N{=}C(CF_3)C(CF_3){=}NCF_3$ (IX)	69.5	8.5	67.6	8.6

Perfluoro-2,5-diazahexa-2,4-diene. The isomerization of $CF_2{=}NCF_2CF_2N{=}CF_2$ (III) to $CF_3N{=}CF{-}CF{=}NCF_3$ (IV) also occurs readily at room temperature. In fact, the bisazomethine III frequently isomerized completely while being stored as a gas in glass bulbs without the addition of cesium fluoride. This was also true to a lesser extent with the formation of the carbodiimide from bisazomethine (I). The fluoride ions in these cases are presumably provided by partial hydrolysis due to adventitious moisture present on the glass.[5]

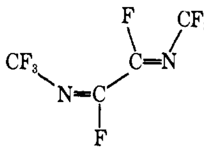
$$\underset{\text{III}}{CF_2{=}NCF_2CF_2N{=}CF_2} \xrightarrow{F^-} \underset{\text{IV}}{CF_3N{=}CFCF{=}NCF_3}$$

Perfluoro-2,5-diazahexa-2,4-diene (IV), bp 58°, was identified by elemental analysis and spectral considerations (see Tables I, II, and IV). The mass spectral patterns of the two isomers, III and IV, are compared in Table III.

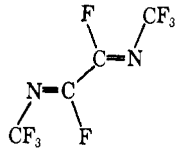
With the exception of bis(trifluoromethyl)carbodiimide, the isomerized bisazomethines are all capable of existing in several geometrically isomeric forms. In some cases, the presence of more than one isomer was observed by F^{19} nmr spectral measurements. Although IV can exist in three possible geometrically isomeric forms, only one isomer was observed.



IVa



IVb



IVc

The structure IVc was assigned to this isomer on the basis of F^{19} nmr considerations. Only a single F–CF_3 coupling constant of 14.2 cps was observed. IVb would show two different coupling constants, whereas the coupling constant for IVa would be small.[6]

The assignment of configuration in the above case and later examples is based on a comparison of the *cis* and *trans* F–F coupling constants with those observed for fluorinated olefins.[6] In general, we have found that the coupling constants across the C=N bond are smaller than those reported for $>C{=}C<$ derivatives.

Perfluoro-(3-methyl-2,5-diazahexa-2,4-diene). The isomerization of $CF_2{=}NCF(CF_3)CF_2N{=}CF_2$ (V) occurs rapidly in the presence of CsF in the gas phase or in $CFCl_3$ solution and slowly in $CFCl_3$ solution without added cesium fluoride.

In the liquid-phase reaction without CsF, both the partially isomerized bisazomethine VI and the fully isomerized material (VII) were obtained in the ratio about 9 to 1. There was no evidence for any partially isomerized bisazomethine in which initial fluoride attack occurred at the $CF_2{=}N$ group adjacent to the carbon bearing the CF_3 moiety.

$$\underset{\text{V}}{CF_2{=}NCF_2CF(CF_3)N{=}CF_2} \xrightarrow{F^-} \underset{\text{VI}}{CF_3N{=}CFCF(CF_3)N{=}CF_2}$$

$$\xrightarrow{F^-} \underset{\text{VII}}{CF_3N{=}CFC(CF_3){=}NCF_3}$$

On the other hand, in the gas phase, with CsF, the isomerization of bisazomethine V to VII was complete within 30 min, and the presence of VI could not be detected.

Perfluoro(3-methyl-2,5-diazahexa-1,4-diene) (VI) exists in two geometric isomeric forms, VIa and VIb, which were observed in the ratio of about 10:1. Although VIa and VIb both possess an asymetric carbon atom, no evidence of optical isomers was detected.

The fully isomerized product VII can theoretically exist in four geometrically isomeric forms, two of

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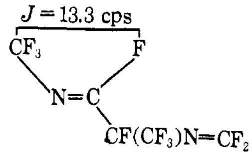
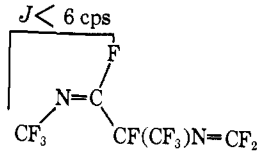
(5) Water is reported not to affect this type of isomerization: R. E. Banks, M. G. Barlow, W. R. Deem, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc.*, 981 (1966).

(6) G. V. D. Tiers, *J. Phys. Chem.*, **66**, 1192 (1962).

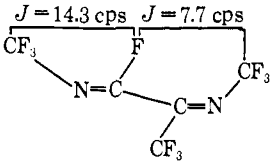


VIa

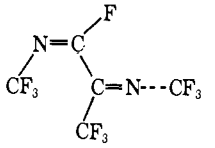


VIb

which, VIIa and VIIb, were observed in the ratio of approximately 15:1 (estimated from the relative peak areas in the F^{19} nmr spectra). Based on the observed splitting of the terminal CF_3 groups into a doublet and



VIIa



VIIb

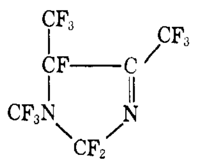
the magnitude of the coupling constants in the F^{19} nmr spectrum, the structure of VIIa is quite certain. Although the structure of VIIb cannot be determined on the basis of spectral considerations because of broadening of the signals and the complex nature of the spectrum, the fivefold splitting (J = 6.0 cps) of the terminal CF_3 group does suggest the partial assignment of configuration shown.

Miller[2] has discussed an S_N2' mechanism for the cesium fluoride catalyzed isomerization of perfluorodienes. In most cases, the mechanism of isomerization of the perfluoro-α,ω-bisazomethines described herein can also be rationalized on the basis of an S_N2' mechanism. Certainly, the isolation of the partially isomerized product VI from the slow isomerization of V in $CFCl_3$ solution, without catalyst, affords strong support for such a mechanism. In some cases, however, as discussed in later sections, cyclic intermediates are indicated.

Perfluoro(3,4-dimethyl-2,5-diazahexa-2,4-diene). Cesium fluoride was necessary to effect the isomerization of $CF_2{=}NCF(CF_3)CF(CF_3)N{=}CF_2$ (VIII) to perfluoro(3,4-dimethyl-2,5-diazahexa-2,4-diene) (IX), presumably by a typical S_N2' mechanism. The identity of IX was established on the basis of its infrared, mass, and F^{19} nmr spectra and elemental analysis. The bisazomethine IX can exist in two possible geometric forms; however, the F^{19} nmr spectrum showed broad and complex signals which could not be resolved and no attempt was made to assign geometric structures.

$$\underset{\text{VIII}}{CF_2{=}NCF(CF_3)CF(CF_3)N{=}CF_2} \xrightarrow{F^-} \underset{\text{IX}}{CF_3N{=}C(CF_3)C(CF_3){=}NCF_3}$$

+



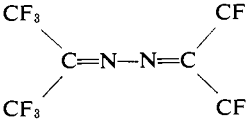
X

The isomerization of VIII with cesium fluoride also resulted in the formation of a minor product (30% yield) identified as perfluoro-(1,4,5-trimethyl-3-imidazoline) (X). The spectral properties of X are described in Tables I, II, and V. A further indication of the cyclic nature of X was obtained from its far-ultraviolet spectrum; whereas conjugated perfluoroazines and bisazomethines all exhibit maxima in their far-ultraviolet spectra (see Table VI), X does not.

Table V. Mass Spectra of V–X

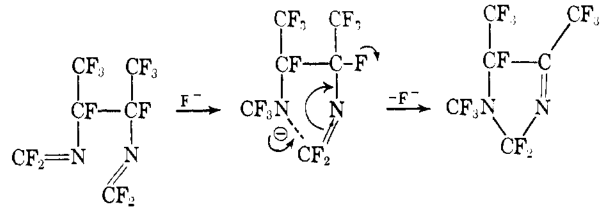
m/e	Assigned ion	Pattern % V	VI	VII	VIII	IX	X
28	N_2	3.1	...	...	1.6	...	1.2
31	CF	14.1	11.2	6.7	17.4	4.3	9.1
50	CF_2	15.1	9.5	5.3	16.8	3.9	5.8
69	CF_3	65.1	100	100	100	100	100
76	C_2F_2N	6.4	4.8	3.0	10.6	3.1	...
95	C_2F_3	6.3	4.4	1.5	9.3	...	2.0
100	C_2F_4	1.4	...	...	2.1	...	...
107	C_3F_3N	...	...	...	1.1	...	...
114	C_2F_4N	100	26.3	5.2	75.1	1.0	9.4
121	$C_3F_3N_2$	1.4	3.4	3.3	2.4	...	1.4
126	C_3F_4N	...	...	...	2.8	1.1	2.3
131	C_3F_5	...	...	...	1.2	...	...
145	C_3F_5N	1.6	1.2	...	3.1	1.1	2.7
164	C_3F_6N	17.8	27.4	12.1	85.2	15.7	21.7
171	$C_4F_5N_2$	1.3	1.5	...	...	...	...
176	C_4F_6N	...	...	...	1.4	...	...
209	$C_4F_5N_2$	3.0	11.7	9.7	...	...	...
214	C_4F_8N	1.5	...	...	...	...	...
221	$C_5H_7N_2$	...	...	...	2.6	2.0	3.8
259	$C_5H_9N_2$	...	...	...	1.7	...	13.7
309	$C_6F_4N_2$	...	...	...	...	...	4.6
Molecular weight		290	279	NA	324	338	323

Table VI. Far-Ultraviolet Spectra

Compound	λ_{max}, mμ	ε, l. mole^{-1} cm^{-1}
$CF_2{=}NN{=}CF_2$	180	7,434
$CF_3N{=}CFCF{=}NCF_3$	181.1	12,640
$CF_3N{=}C(CF_3)C(CF_3){=}NCF_3$	195.9	1,880
	195.9	1,376
$CF_3NCF(CF_3)C(CF_3){=}NCF_2$	No maxima >170 mμ	

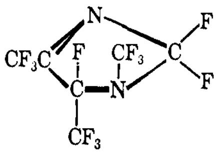
[a] This material was prepared by the method suggested by W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **30**, 1398 (1965).

The formation of the cyclic isomer during the CsF-catalyzed isomerization of VIII is rationalized on the basis of the following mechanism involving cyclization *via* the initially formed nitrogen anion.

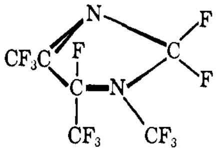


VIII X

The imidazoline X is capable of existing in two geometrically isomeric forms, Xa and Xb. The F^{19} nmr spectrum showed the presence of only one of the isomers. No assignment of the structure could be made since the broadening of the F^{19} nmr signals caused by the nitrogen atoms rendered their fine structure unob-



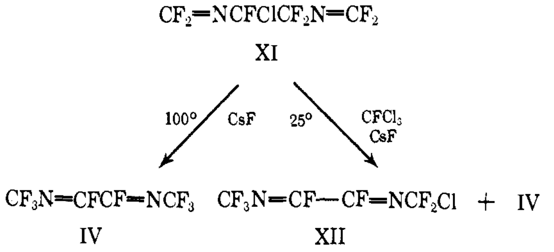
Xa



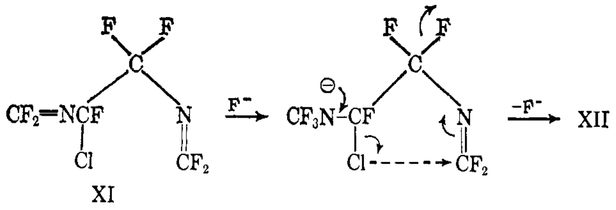
Xb

tainable. However, steric factors, as exemplified by molecular models, strongly favor structure Xa.

Isomerization of Perfluoro(3-chloro-2,5-diazahexa-1,5-diene) (XI). The isomerization of XI was examined both in $CFCl_3$ solvent at room temperature and at 100° in the absence of solvent using cesium fluoride catalyst. Heating XI at 100° in the presence of CsF resulted in essentially complete conversion to IV, as expected on the basis of the nature of chloride ion compared with fluoride ion as a leaving group in related perhaloalkenes.[7]



On the other hand, in $CFCl_3$ solvent at room temperature, XI is slowly isomerized over a period of weeks to a mixture of XII and IV. The ratio of products was 2:1 favoring the chloro-substituted bisazomethine, XII. It is possible that XII is formed *via* a cyclic path as shown below.



It is recognized that the formation of XII as the major[7] product implies a preference for initial fluoride attack to occur at the $CF_2{=}N$ moiety adjacent to the CFCl group. This preference is not in agreement with the expected azomethine reactivity as based on chlorine and fluorine electronegativities but could possibly be rationalized on the basis of the desirability of chloride ion as a leaving group.

In conclusion, it should be stated that, although no accurate measurements of the rates of isomerization were obtained, it is apparent that the relative rates of isomerization are $CF_2{=}NCF_2 > CF_2{=}NCF(CF_3){-} > CF_2{=}NCFCl{-}$.

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. 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^*[8] values at a dilution of 10–25%. Trifluoroacetic acid is $\phi^*76.5$ on this scale. Mass spectra were measured 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. 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.

Isomerizations were achieved by condensing reactants into a small glass bulb *in vacuo* at -196° and allowing them to warm to room temperature. When cesium fluoride was used it was dried prior to use by heating it at 200° *in vacuo*.

The following example describing the isomerization of perfluoro-(3-methyl-2,5-diazahexa-1,5-diene) is typical and serves to illustrate the general procedures utilized.

Perfluoro(3-methyl-2,5-diazahexa-1,5-diene). Perfluoro(3-methyl-2,5-diazahexa-1,5-diene) (0.2 g) and trichlorofluoromethane (0.5 g) were condensed at -196° *in vacuo* into an nmr tube. The tube was then sealed and allowed to warm to room temperature. At this time, F^{19} nmr spectral measurements indicated only the presence of unreacted perfluoro-α,ω-bisazomethine. Over a period of 14 days, the contents of the tube slowly isomerized to perfluoro-(3-methyl-2,5-diazahexa-1,4-diene) (90%) and perfluoro(3-methyl-2,5-diazahexa-2,4-diene) (10%), as indicated by repeated F^{19} nmr spectral measurements. The contents of the tube were then transferred to a vacuum system, separated by vapor phase chromatography, and identified by their spectral properties which are reported in the tables.

A further sample of perfluoro(3-methyl-2,5-diazahexa-1,5-diene) (0.2 g) and trichlorofluoromethane (0.5 g) was condensed into an nmr tube containing cesium fluoride (0.1 g). After the tube and its contents had warmed to room temperature, F^{19} nmr spectral measurements indicated that quantitative isomerization had occurred to perfluoro(3-methyl-2,5-diazahexa-2,4-diene) which was purified by vapor phase chromatography and identified by elemental analysis and spectral properties which are shown in the tables.

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(7) W. T. Miller, J. H. Fried, and H. Goldwhite, *J. Am. Chem. Soc.*, **82**, 3091 (1960).

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