ous dimethylamine containing *ca.* 0.1 g. of copper powder. After 5 hr. of stirring the layers were separated and the aqueous layer was extracted with two 50-ml. portions of ether which were added to the organic portion. The ethereal solution was dried over anhydrous potassium carbonate. Distillation gave 19.5 g. (56% yield), b.p. 80–84° (70 mm.), $n^{25}D$ 1.4440.

The methiodide (IV, Table I) was prepared from 12.9 g. (0.1 mole) of the amine and 21.3 g. (0.15 mole) of methyl iodide in 50 ml. of ethyl acetate. The product was collected by filtration and washed with acetone. The crude material (14.2 g., 52% yield) had m.p. 135–137°. Crystallization from methylene dichloride gave material with m.p. 142–144°.

Preparation of 1-Chloro-3-ethyl-2-pentene.—Dry hydrogen chloride was bubbled through 57 g. (0.5 mole) of 3-ethyl-1-penten-3-ol[10] with stirring while the temperature was maintained at 25–30° until 18 g. (0.5 mole) of hydrogen chloride had been taken up. The layers were separated and the organic portion was dried over anhydrous potassium carbonate. Distillation gave 39 g. (59% yield), b.p. 90–95° (112 mm.). Redistillation gave material with b.p. 78–79° (56 mm.), $n^{25}D$ 1.4513. The infrared spectrum showed no peaks at 7.1 μ characteristic of the $=CH_2$ in-plane deformation nor was there a peak at 10 μ characteristic of the =CH out-of-plane deformation in vinyl groups. There was, however, a strong peak at 6.05 μ assigned to the C=C stretch and a peak at 11.65 μ assigned to the =CH out-of-plane deformation. The p.m.r. spectrum showed a triplet at τ 4.9 with J = 7.5 c.p.s. (0.82 proton), a doublet at τ 6.1 with J = 7.5 c.p.s. (2 protons), two overlapping quartets at about τ 7.9 with J = 7.5 c.p.s. (3.9 protons), and a triplet at τ 9.01 with J = 7.5 c.p.s. (6.2 protons). The quartets assigned to the methylene protons within the ethyl groups have slightly different chemical shifts due to the fact that one is *cis* to the chloromethylene group and is deshielded by the chlorine atom. The quartet at higher field is slightly less intense probably due to small long-range spin–spin splitting by the olefinic proton.

Preparation of 1-Dimethylamino-3-ethyl-2-pentene Methochloride.—To 11.1 g. (0.075 mole) of 40% trimethylamine in acetone solution was added dropwise with stirring 6.6 g. (0.05 mole) of 1-chloro-3-ethyl-2-pentene. After 1 hr. the mixture was cooled to 10° and the product was collected by filtration. The crude product (4.4 g., 46% yield) had m.p. 204–205°. Crystallization from acetone plus acetonitrile gave material with m.p. 206–207°.

The compound was also prepared by hydrogenating 19.0 g. (0.1 mole) of 1-dimethylamino-3-ethyl-1,2-pentadiene methochloride (VI) in 55 ml. of ethanol containing 2 g. of Raney nickel (wet with ethanol) at an initial pressure of 50 p.s.i.g. The catalyst was removed by filtration and the solvent was removed by vacuum distillation. The crude solid weighed 17 g. Recrystallization from acetone plus acetonitrile gave material with m.p. 205–207°. A mixture melting point with the material described above showed no depression and the infrared spectra were superimposable.

Preparation of Methiodides from Methochlorides.—A boiling solution of 7.5 g. (0.05 mole) of sodium iodide in 20 ml. of acetonitrile was added to a boiling solution of 8.1 g. (0.05 mole) of 3-dimethylamino-3-methyl-1-butyne methochloride (I) in 80 ml. of acetonitrile. The resulting mixture was filtered hot and the solvent was removed on a rotary evaporator. The residue, crystallized from ethanol, had m.p. 205–207° dec.; lit.[11] m.p. 210° dec.

1-Dimethylamino-3-ethyl-1,2-pentadiene methiodide was prepared in a similar manner from 8 g. (0.05 mole) of sodium iodide and 9.5 g. (0.05 mole) 1-dimethylamino-3-ethyl-1,2-pentadiene methochloride (VI). The product (10.3 g., 54% yield) crystallized from ethyl acetate plus acetone had m.p. 137–139°.

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Reaction of Amines with Cyclic Fluorinated Olefins[1,2]

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A series of perfluoro- and per(chlorofluoro)cycloalkenes was treated with methylamine and ethylamine to give 1-alkylamino-2-chloro- (or fluoro-) 3-alkyliminopolyfluorocycloalkenes which were hydrolyzed to the corresponding amino ketones. The same series of olefins also reacted with hydroxylamine to give 1,2,3-trioximinopolyfluorocycloalkanes. A monooxime was isolated and shown to be an intermediate in the trioxime formation. The 1-methylamino-2-chloro- (or fluoro-) 3-alkyliminopolyfluorocycloalkenes reacted with ethylamine and hydroxylamine and a methylamino group was replaced by an ethylamino and hydroxylamino group, respectively. Mechanisms for these reactions are presented.

Several examples of the reaction[3] of polyfluorinated cyclic olefins with primary amines,[3–6] secondary[4,7–9] amines, and ammonia have been reported.[4–6] With secondary amines, monosubstitution in a vinylic position was obtained, but with primary amines and ammonia only iminoamines were isolated. Addition–elimination and SN2′ mechanisms have been proposed to account for the products.

We now report a comprehensive study of the reaction of five cyclic olefins (I–V) with primary alkylamines and the more nucleophilic but sterically similar hydroxylamine.

Reactions with Methylamine and Ethylamine.—The cyclic olefins I–V reacted with gaseous methylamine and III and IV with gaseous ethylamine to give the iminoamines VI–XI, which were hydrolyzed on a chromatography column packed with acid-washed alumina to give the 1,3-amino ketones XII–XVII. The 1,3-iminoamines and the 1,3-amino ketones were

(1) This paper is based on a thesis submitted by J. J. Turner to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Presented at the Third International Symposium of Fluorine Chemistry, Munich, Sept. 1965.

(3) R. L. Pruette, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *J. Am. Chem. Soc.*, **72**, 3646 (1950).

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colorless crystalline solids which decomposed slowly at room temperature even in an evacuated desiccator over concentrated sulfuric acid, potassium hydroxide pellets, or Drierite. They were, however, stable for extended periods at −10° in stoppered vials under nitrogen. Their structures were determined from their spectral data (Tables I–IV) and elemental analyses (Table V).

TABLE I

INFRARED ABSORPTIONS OF THE AMINO AND OXIMINO PRODUCTS[a]

Compd.	Absorption, μ: NH or OH	CH	C=O	C=C	C=N
VI	3.12	3.50		5.95	6.10
VII	3.12	3.50		6.10	6.10
VIII	3.11	3.38		5.91	6.14
IX	3.15	3.40		6.20	6.20
	2.98[b]			6.11[b]	6.11[b]
X	3.12	3.50		5.95	6.18
XI	3.12	3.40		6.16	6.00
XII	3.10	3.34	5.55	6.20	6.20
	3.28	3.41			
XIII	3.03		5.61	6.10	6.10
	3.20				
XIV	3.10	3.40	5.77	6.22	6.22
	3.25				
	3.30				
XV	3.08		5.81	6.22	6.11
	3.17[b]		5.81[b]	6.22[b]	6.11[b]
XVI	3.08		5.79	6.20	6.20
	3.22				
XVII	3.08	3.42	5.81	6.30	6.07
XVIII	3.07				6.10
XIX	3.00				6.10
XX		3.36			6.22
		3.42			
		3.52			
XXI		3.37			6.13
		3.42			
		3.48			
		3.56			
XII	2.81, 3.06			6.29	6.11
XXIII	2.92, 2.95	3.42		5.95	6.09
	3.05				
XXIV	3.10	3.39		6.12	6.12

[a] Fluorolube–Nujol mulls. [b] Taken from ref. 4.

TABLE II

PROTON N.M.R. DATA OF THE AMINO AND OXIMINO PRODUCTS

Compd.	H¹ p.p.m. below TMS: CH_3	CH_2	NHR[a]	$NHOH$	$NHOH$	C=NHOH
VI[b]	3.12					
VII[b]	3.16					
VIII[b]	3.38		4.74			
IX[b]	3.38		5.66			
X[b]	1.27	3.62	4.80			
XI[b]	1.29	3.70	4.90			
XII[b]	3.16, 3.23					
XIII[b]	3.17, 3.27[c]					
XIV[b]	3.20, 3.30[c]					
XV[b]	3.30, 3.44[c]					
XVI[b]	1.37	3.69	3.30			
XVII[b]	1.23, 1.38[c]	3.75	5.56			
XVIII[d]						11.30
XIX[d]						12.05
XX[f]	4.22, 4.19[c]					
XXI[e]	4.27, 4.22[c]					
XXII[e]						9.34
XXIII[f]	3.07, 3.13[c]			6.10	1.09	10.44
XXIV[f]	3.08, 3.15[c]			6.10	1.07	10.46

[a] Shifts to higher field on dilution. [b] 10% solution in chloroform. [c] Tautomeric mixture. [d] 10% solution in methanol. [e] 10% solution in carbon tetrachloride. [f] 10% solution in chloroform–acetone.

TABLE III

FLUORINE N.M.R. DATA OF THE AMINO AND OXIMINO PRODUCTS

Compd.	F¹⁹ p.p.m. above trifluoroacetic acid[a]: =CF—	CF_2
VI[b]	57.8	38.1
VII[b]		33.1
VIII[b]	77.7	38.4
IX[b]		35.6
X[b]	77.0	38.5
XI[b]		36.6
XII[b,c]	54.2, 56.7	33.9, 38.8
XIII[b,c]		33.1, 37.4
XIV[b,c]	83.2, 86.3	37.6, 40.8
		46.3, 48.1
XV[b,c]		37.8, 39.2
		46.0, 47.7
XVI[b,c]	83.6, 86.6	36.9, 40.3
		47.2, 48.5
XVII[b,c]		38.2, 43.1
		47.2, 48.8
XVIII[d]		30.8
XIX[d]		37.8, 40.5
XII[e]		37.0, 40.4
XXII[e]		37.6, 41.4
XXIII[f,c]	76.5, 79.6	36.0, 37.7
		39.9, 41.0
XXIV[f,c]		34.8, 36.7
		39.4, 40.8

[a] External standard. [b] 10% solution in chloroform. [c] Tautometric mixture. [d] 10% solution in methanol. [e] 10% solution in carbon tetrachloride. [f] 10% solution in chloroform–acetone.

TABLE IV

ULTRAVIOLET ABSORPTIONS OF THE AMINO AND OXIMINO PRODUCTS

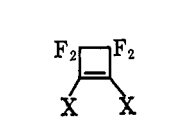
Compd.	Absorption, mμ (ε): Abs. ethanol	0.1 *N* HCl	0.1 *N* NaOH
VI	263 (26,600)	275 (32,000)	265 (27,800)
VII	265 (26,600)	277 (30,600)	267 (28,800)
VIII	287 (22,000)	316 (38,000)	292 (33,000)
IX	290 (28,200)	318 (36,700)	293 (25,200)
X	289 (30,200)		
XI	291 (29,400)		
XII	253 (32,500)	256 (30,600)	
XIII	255 (24,600)	259 (25,200)	
XIV	285 (34,500)	291 (34,700)	
XV	289 (30,400)	295 (30,400)	
XVI	287 (34,400)		
XVII	289 (29,500)		
XVIII	216 (9850)		
	293 (9500)		
XIX	228 (17,900)		
	282 (7700)		
XX	226 (11,500)		
	313 (16,900)		
XXI	237 (16,800)		
	299 (9700)		
XXII	247 (21,200)		
XXIII	285 (33,200)		
XXIV	286 (30,400)		

As Parker[4] has already shown for IX, the 1,3-iminoamines VI–XI and 1,3-amino ketones XII–XVII had ultraviolet absorptions in ethanol that were at longer wave lengths than normally found for C=C—C=N,

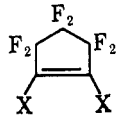
Table V
Elemental Analyses

Compd.	Calcd., % C	H	Cl	F	N	Found, % C	H	Cl	F	N
VI	43.91	4.30		34.73	17.07	44.08	4.27		34.92	17.28
VII	39.91	3.91	19.63	21.04	15.51	40.04	3.94	19.75	21.21	15.33
VIII	39.27	3.29		44.63	13.08	39.63	3.40		43.68	12.60
X	44.63	4.58		39.22	11.57	44.79	4.47		39.00	11.87
XI	41.79	4.29	13.71	29.38	10.83	41.91	4.20	13.90	29.50	11.09
XII	39.75	2.67		37.72	9.32	39.75	2.64		37.43	9.37
XIII	35.84	2.41	21.16	22.68	8.40	36.00	2.73	21.29	22.90	8.61
XIV	35.83	2.01		47.24	6.97	35.66	1.87		47.59	7.17
XVI	39.08	2.81		44.16	6.51	39.23	2.89		44.42	6.39
XVII	36.31	2.61	15.31	32.82	6.05	36.45	2.78	15.49	32.79	6.00
XVIII	26.83	1.69		21.22	23.46	27.37	2.08		20.42	23.05
XIX	26.21	1.32		33.17	18.34	26.52	1.10		32.79	18.46
XX	38.01	4.10		17.18	19.00	38.10	4.11		17.00	18.77
XXI	35.43	3.35		28.02	15.50	35.48	3.41		27.98	15.65
XXII	25.24	0.42	29.80	31.93	5.88	25.42	0.46	29.56	31.59	6.02
XXIII	33.33	2.31		43.98	12.96	33.76	2.43		44.13	12.94
XXIV	30.97	2.15		32.69	12.04	31.76	1.98		33.40	12.13

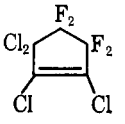
N=C—C=N, N=C—C=O, or C=C—C=O linkages. Similar to Parker's findings for IX, a bathochromic shift was observed in acid or basic media in all cases. This can be accounted for only by a 1,3 structure for compounds VI through XVII (although VI has been previously reported as 1,2[3]), since only in the 1,3 structure is the amino nitrogen attached to the end of a conjugated system. The nonbonded pair of electrons of nitrogen provides additional resonance stabilization of the excited state, lowering its energy relative to the ground state,[10] and thus giving the observed shift. The high symmetry of the 1,3-iminoamines would be expected to enhance their resonance stabilization, and this was perhaps reflected in that their bathochromic shifts were larger than those of the 1,3-amino ketones and were larger in acid or base than in the neutral ethanol.



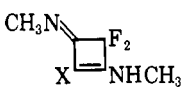
I, X = F
II, X = Cl



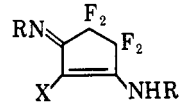
III, X = F
IV, X = Cl



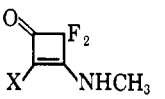
V



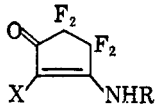
VI, X = F
VII, X = Cl



VIII, X = F; R = CH_3
IX, X = Cl; R = CH_3
X, X = F; R = C_2H_5
XI, X = Cl; R = C_2H_5



XII, X = F
XIII, X = Cl



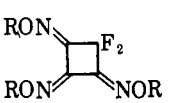
XIV, X = F; R = CH_3
XV, X = Cl; R = CH_3
XVI, X = F; R = C_2H_5
XVII, X = Cl; R = C_2H_5

The single methyl resonance in the proton n.m.r. and the single difluoromethylene resonance in the fluorine n.m.r. of the iminoamines VI–XI further justifies the 1,3 structure and indicates the rapid tautomeric proton equilibrium noted already by Parker for IX.[4] The two methyl, the vinyl fluorine, and the difluoromethylene resonances observed in the spectra of the 1,3-amino ketones XII–XVII show the presence of a keto–enol mixture, the ratio of which in all cases was about 1:1 as determined by peak areas.

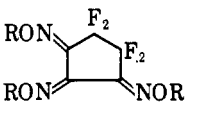
An attempt was made to isolate a monoimino intermediate, but reaction of V at 0°, which was relatively slow, gave only starting material and the iminoamine IX.

Reaction with Hydroxylamine.—Very few examples of addition of hydroxylamine to halogenated olefins have been reported. Knunyants[11] prepared 2H-polyfluorohydroxamic acid fluorides from perfluoropropene and -isobutylene using hydroxylamine, and McBee[12] has synthesized 1,2,3,4-tetrachlorocyclopentadienone oxime from hexachlorocyclopentadiene.

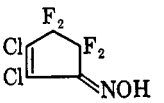
We now report that the reaction of the olefins I–IV with hydroxylamine in methanol gave 1,2,3-trioximinopolyfluorocycloalkanes XVIII and XIX, which were derivatized by conversion to the corresponding 1,2,3-tris(methoximino)polyfluorocycloalkanes XX and XXI using diazomethane. The trioximes XVIII and XIX



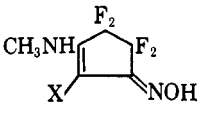
XVIII, R=H
XX, R=CH_3



XIX, R=H
XXI, R=CH_3



XXII



XXIII, X=F
XXIV, X=Cl

were amorphous powders that decomposed at their melting points with evolution of a brown gas; the decomposition points were a function of the rate of heating

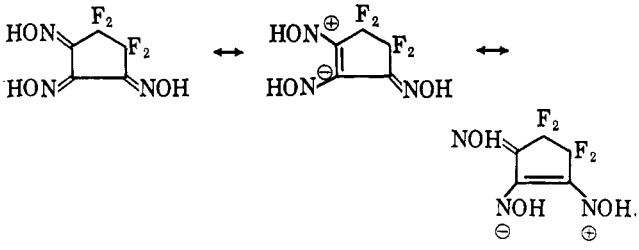
(10) (a) L. N. Ferguson, "The Molecular Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964, pp. 498–510; (b) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 307.

(11) I. L. Knunyants, E. G. Pervalova, and V. N. Frosin, *Proc. Acad. Sci. USSR, Chem. Sect.*, **127**, 535 (1959).

(12) E. T. McBee, U. S. Patent 3,141,043 (July 14, 1964); *Chem. Abstr.*, **61**, 8205*f* (1964).

and were somewhat difficult to reproduce. The trioximes decomposed on treatment with mineral acids liberating carbon dioxide and were themselves strong acids (pH 1 in 10% aqueous solution). They appeared to complex in oxygenated solvents, which caused problems in the purification (see Experimental Section).

Structural assignments were based on elemental analyses and spectral data (Tables I–V). For the oximes XVIII and XIX, elemental analyses and infrared and n.m.r. spectra indicate three oxime groups, and analyses and proton n.m.r. showed the presence of three methyl groups in the trioxime ethers XX and XXI. The ultraviolet spectra of the trioximes and trioxime ethers had two characteristic absorptions; the shorter wave length one was assigned to a 1,2-dioximino linkage and the longer to the 1,3 conjugation similar to that observed in the 1,3-iminoamines.



The trioxime ethers were shown to have an O-methyl ether structure because hydrolysis and treatment of the hydrolysate with Fehling's solution gave no precipitate. The isomeric nitrone would have given N-methylhydroxylamine on hydrolysis, and this is easily oxidized by Fehling's solution.

Reaction of V with hydroxylamine gave the monooxime XXII, analogous to the monoimine sought earlier. The chemical and physical data (Tables I–V) could only be accounted for by the monooxime XXII which was shown to be an intermediate in the formation of trioxime by conversion to XIX with excess hydroxylamine. The formation of the same trioxime from IV and V was excellent confirmation of the 1,2,3-trioxime structure.

An examination of the stoichiometry of trioxime formation revealed the necessity for an oxidation step and it was assumed that a hydroxylamino group was oxidized to an oximino group by either hydroxylamine or oxygen, at some stage between monooxime and trioxime formation. A kinetic experiment in which the reaction course was followed by the absorbance in the ultraviolet spectra of the mono- and the trioxime determined that the trioxime was formed at approximately the same rate regardless of the presence or absence of oxygen. Thus, hydroxylamine must have been the oxidizing agent.

Further Reaction of 1,3-Iminoamines with Amines.—The 1,3-iminoamines VIII and IX were treated with excess hydroxylamine and another primary alkylamine, ethylamine. No trisubstituted products could be isolated.

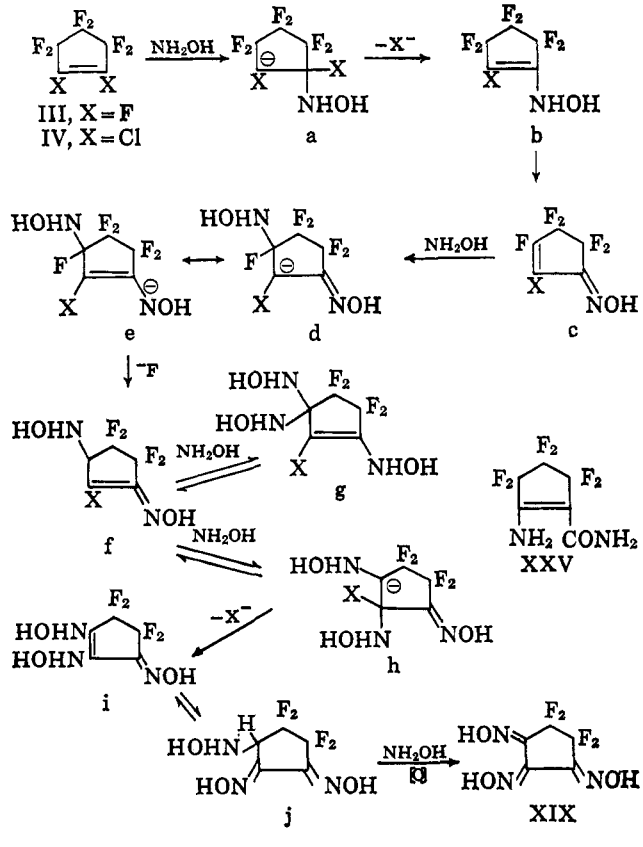
Reaction of IX with excess methylamine at 65° gave only IX and degradation. However, when VIII and IX were treated with ethylamine, the methylamino and -imino groups were replaced by the respective ethyl groups. The crude reaction products could not be crystallized, but infrared and proton n.m.r. spectra indicated the presence of both methyl- and ethylamino and -imino groups. Chromatographic hydrolysis gave the 1,3-ethylamino ketones XVI and XVII, respectively.

A similar reaction was observed when VIII and IX were treated with hydroxylamine, giving the compounds XXIII and XXIV. These were identified by analytical and spectral data (Tables I–V) using arguments similar to those advanced for the 1,3-iminoamines VI–XI and the 1,3-amino ketones XII–XVII. Proton n.m.r. again indicated a tautomeric equilibrium in which the ratio of the oximino to hydroxylamino forms was about 60:40.

When VIII and IX were treated with excess hydroxylamine under more vigorous conditions, VIII still gave only XXIII, but IX reacted further giving the trioxime XIX as well as XXIV. This result is surprising, as in this work the fluoro olefins reacted more rapidly than those with vinylic chlorine. Conceivably, chloride ion being a better leaving group than fluoride ion was the decisive factor in this instance.

Mechanistic Considerations.—From the foregoing data, it appears that the reactions of the fluorinated cyclic olefins with primary alkylamines and hydroxylamine proceed by similar mechanisms. The isolation of the monooxime XXII analogous to the monoimine proposed by Parker[4] supports this. Further, the reactions of the 1,3-iminoamines VIII and IX with ethylamine and hydroxylamine appear to proceed by the same mechanism, as the same type of exchange reaction occurs in each case. Thus, a mechanism can be proposed for the formation of the trioximes XVIII and XIX, as exemplified in Chart I, starting from III and IV.

CHART I



First, hydroxylamine adds to the olefin, forming the inductively stabilized anionic intermediate a. This eliminates halide ion from the carbon bonded to the hydroxylamino group to give b, as fluoride ion is reluctant to leave from the more electron-deficient difluoromethylene group. Mill's[5] isolation of the monoamino intermediate XXV provides an analogy for b. An undoubtedly rapid 1,4 elimination from b gives the monooxime c, evidence for which is given by the isolation of XXII. Further amine attack is at the carbon bonded to fluorine and gives the resonance-stabilized anion d–e. This reaction may be rationalized as attack at the most positive carbon atom[13] or as attack at that carbon resulting in the most stable anion.[14] Elimination of fluoride ion then gives the 1,3-disubstituted intermediate f, which was not isolated but is clearly analogous to the 1,3-iminoamines.

The next step is thought to involve attack at the carbon atom bonded to hydroxylamino group for the reasons given in the preceding paragraph, leading to the 1,3,3-trisubstituted intermediate g upon proton acceptance. That this is an equilibrium is suggested by the exchange reactions of VIII and IX with ethylamine and hydroxylamine, and the failure to isolate any 1,3,3-trisubstituted derivatives like g indicates that f → g is unfavorable. Thus, although it is reasonable to postulate attack at the carbon bonded to the hydroxylamino group, it essentially leads to no further reaction. Attack on the carbon bonded to the vinyl halogen leads to the intermediate h, which is perhaps unfavorable to some extent, and therefore the primary alkylamines do not react whereas the more nucleophilic hydroxylamine does. The intermediate h can eliminate either hydroxylamine regenerating f or halide giving the 1,2,3-trisubstituted intermediate i. This explanation can be used to rationalize why XXIV gave the trioxime XIX whereas XXIII did not. Presumably, in the anion from XXIV, chloride eliminates in preference to hydroxylamino, but in that from XXIII, hydroxylamino eliminates instead of fluoride, giving the appearance of no reaction. In view of the tautomeric nature of the iminoamines, the amino ketones, and the oximinoamines, it is assumed that i also exists as the tautomers i and j and the latter is oxidized to the trioxime XIX. Oxidation is the final step as the vinyl hydroxylamino groups in the 1,3-hydroxylaminoimines XXIII and XXIV are stable towards oxidation, and this suggests that an alkyl hydroxylamino group is necessary as in j for oxidation to occur. Thus, if f is accepted, the oxidation cannot occur before the formation of the 1,2,3-trisubstituted intermediate.

The relation of this work to other nucleophilic substitutions on cyclic fluorinated olefins is interesting. The general pattern given for alkoxides,[15,16] lithium aluminum hydride,[13] and methyllithium[17] based on addition–elimination mechanisms is still operative but with an important modification.

(13) D. E. M. Evans, W. J. Feast, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 4828 (1963).

(14) J. D. Park, J. R. Dick, and J. H. Adams, *J. Org. Chem.*, **30**, 400 (1965).

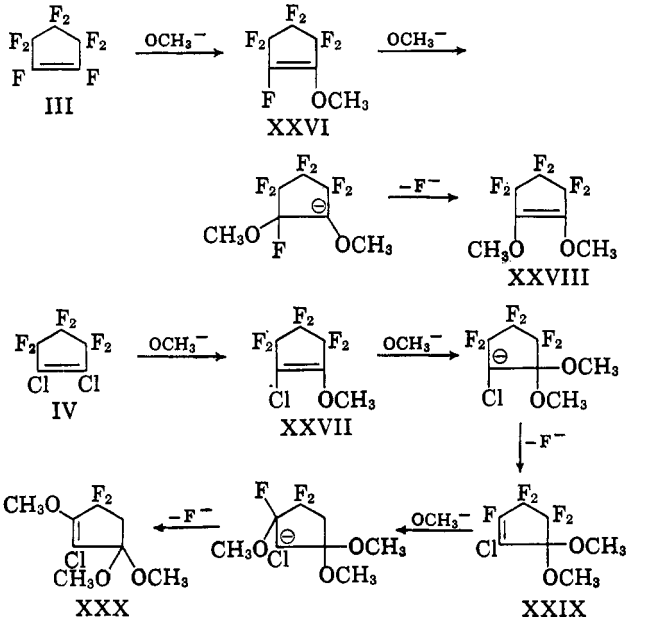
(15) R. F. Stockel, M. T. Beachem, and F. H. Megson, *Can. J. Chem.*, **42**, 2880 (1964).

(16) E. T. McBee, D. L. Crain, R. D. Crain, L. R. Belohlav, and H. P. Braendlin, *J. Am. Chem. Soc.*, **84**, 3557 (1962).

(17) D. R. Sayers, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 3035 (1964).

For example, reaction of alkoxide with III and IV gives the monoalkoxy derivatives XXVI[15] and XXVII,[16] respectively. The next step involving attack to give the most stable anion, or at the most positive carbon atom, results in vinylic substitution for XXVI giving XXVIII[15] and an allylic substitution for XXVII giving XXIX.[16] In addition, XXVIII does not react further whereas XXIX does, giving XXX (see Chart II).

Chart II



It is considered highly probable that the amine reactions with III and IV (and with I, II, and V) give monoamine intermediates,[4,5] but two competitive reaction paths are now available, namely, further attack by amine and elimination of hydrogen fluoride. Since both III and IV give 1,3-iminoamines, it appears that the elimination is the faster process and this determines the structure of the final product.

Experimental Section[18]

1,2-Dichlorohexafluorocyclopentene (IV) was obtained from Hooker Chemical Corp.

1-Chlorotrifluoroethylene and **1,1-dichlorodifluoroethylene** were obtained from Matheson Coleman and Bell.

Hexafluorocyclobutene (I) was prepared in 66% yield from 1-chlorotrifluoroethylene according to the procedure of Rapp and coworkers.[3]

1,2-Dichlorotetrafluorocyclobutene (II) was prepared in 39% yield from 1,1-dichlorodifluoroethylene according to the procedure of Henne.[19]

Octafluorocyclopentene (III) was prepared in 75% yield from 1,2-dichlorohexafluorocyclopentene according to the procedure of Maynard.[20]

(18) All melting points are corrected. Analyses were performed by Mrs. C. S. Yeh, Purdue University. Infrared spectra were recorded using a Beckman Model I.R.-8, and the ultraviolet spectra using a Bausch and Lomb Spectronic 505 spectrophotometer. Vapor phase chromatograms were determined with an Aerograph Autoprep Model A-700 using a 5-ft., 0.25-in. diameter stainless steel column containing 20% GESF-96 Silicone Oil on 60–80-mesh firebrick. Proton n.m.r. spectra were recorded by Mr. W. E. Baitinger, Purdue University, using a Varian Associates Model A-60 spectrometer. Fluorine n.m.r. spectra were recorded by Mr. Baitinger using a Varian Associates Model V-4311 spectrometer operating at 56.4 Mc., using the audio side-band calibration technique.

(19) A. L. Henne and R. H. Ruh, *J. Am. Chem. Soc.*, **69**, 279 (1947).

(20) J. T. Maynard, *J. Org. Chem.*, **28**, 112 (1963).

1,2,3,3-Tetrachlorotetrafluorocyclopentene (V) (with D. H. Campbell[21]).—Finely powdered aluminum chloride (133 g., 1 mole) was added in small portions over 8 hr. to rapidly stirred IV at room temperature, and the mixture was stirred for an additional 13.5 hr The olive green mixture was then poured on ice and the organic layer was separated. The aqueous layer was washed with ether and the organic fractions were combined and dried (Drierite). Distillation through an 18-in. column packed with helices gave ether, recovered IV (45.8 g., 19%), and 1,2,3,3-tetrachlorotetrafluorocyclopentene (V) (16.1 g., 7%): b.p. 155°; $n^{20}D$ 1.4452; λ_{max}^{EtOH} 216.5 mμ (ε 9550); λ_{max}^{neat} 6.20 (m), 7.68 (s), 7.84 (s), 8.30 (m), 8.44 (w), 8.80 (s) (broad), 9.58 (w), 10.60 (w), 11.78 (s), 11.94 (s), 12.48 (s), 14.04 (w) μ. The F^{19} n.m.r. spectrum displayed a pair of triplets, area ratio 1:1, centered at 35.2 and 38.1 p.p.m. above CF_3CO_2H used as external standard.[22]

Anal. Calcd. for $C_5Cl_4F_5$: C, 21.64; H, 0.00. Found: C, 21.90; H, 0.30.

The mass balance from the reaction was mainly hexachlorodifluorocyclopentene and octachlorocyclopentene.

Reaction of Hexafluorocyclobutene with Methylamine (Procedure A).—Hexafluorocyclobutene (I, 18.5 g., 0.12 mole) in 400 ml. of anhydrous ether was cooled to 0° with stirring and treated with excess methylamine added from a cylinder at a rate sufficient to maintain reflux (of methylamine) under a Dry Ice condenser for 1 hr. The methylamine hydrofluoride was filtered and the solution was evaporated to give light yellow crystals of 1-methylamino-3-methyliminotrifluorocyclobutene (VI) (11.5 g., 58%), m.p. 113–118° dec. Three recrystallizations from THF raised the melting point to 113–115° dec.

Reaction of 1,2-Dichlorotetrafluorocyclobutene (II) with Methylamine.—Using procedure A, II (10.0 g., 0.051 mole) in 250 ml. of ether, after 2 hr. at 0°, gave light yellow crystals of 1-methylamino-2-chloro-3-methyliminodifluorocyclobutene (VII), 6.4 g. (69%), m.p. 150–160°. Four recrystallizations from chloroform raised the melting point to 159–160°.

Reaction of Octafluorocyclopentene (III) with Methylamine.—Using procedure A, III (21.2 g., 0.10 mole) in 450 ml. of ether, after 5 hr. at 0°, gave colorless crystals of 1-methylamino-3-methyliminopentafluorocyclopentene (VIII), 21.4 g. (100%), m.p. 103–106°. Recrystallization from hexane raised the melting point to 104–106°.

Reaction of Octafluorocyclopentene (III) with Ethylamine.—Using procedure A, III (5.30 g., 0.025 mole) and ethylamine (11.2 g., 0.25 mole) in 200 ml. of ether, after 2 hr. at 0°, gave crude product. Recrystallization from hexane gave colorless crystals of 1-ethylamino-3-ethyliminopentafluorocyclopentene (X), 4.1 g. (72%), m.p. 63–65°. Four recrystallizations from hexane raised the melting point to 64–65°.

Reaction of 1,2-Dichlorohexafluorocyclopentene (IV) with Methylamine.—Using procedure A, IV (50.0 g., 0.20 mole) in 250 ml. of ether, after 5 hr. at room temperature, gave colorless crystals of 1-methylamino-2-chloro-3-methyliminotetrafluorocyclopentene (IX), 44.5 g. (95%), m.p. 90–92° (lit.[4] m.p. 89–90°).

Reaction of 1,2-Dichlorohexafluorocyclopentene (IV) with Ethylamine.—Using procedure A, IV (6.1 g., 0.025 mole) and ethylamine (11.2 g., 0.25 mole) in 200 ml. of ether, after 4 hr. at room temperature, gave colorless crystals of 1-ethylamino-2-chloro-3-ethyliminotetrafluorocyclopentene (XI), 6.1 g. (100%), m.p. 50–52°. Two recrystallizations from hexane raised the melting point to 52–54°.

Reaction of 1,2,3,3-Tetrachlorotetrafluorocyclopentene (V) with Methylamine at 0°.—1,2,3,3-Tetrachlorotetrafluorocyclopentene (V) (5.0 g., 0.0175 mole) in 100 ml. of anhydrous ether was cooled to −78° and methylamine (1.55 g., 0.052 mole) in 100 ml. of anhydrous ether cooled to −78° was added over a period of 10 min. with stirring. After 2 hr. at −78°, no amine hydrochloride had precipitated (no reaction), and the solution was allowed to warm to 0° over 4 hr. and stirred for 2 hr. at this temperature. Methylamine and 50 ml. of ether were removed *in vacuo* (oil pump) at 0°. The remaining ether solution was filtered and evaporated, and the starting material was recovered by vacuum transfer to a Dry Ice trap, giving 2.15 g. (43%), identified by its v.p.c. retention time. Vacuum distillation of the residue gave a colorless oil, b.p. 81–83° (0.5 mm.), which solidified to a tan solid on standing overnight at room temperature *in vacuo*. Vacuum sublimation (30° and 0.55 mm.) gave yellow crystals of 1-methylamino-2-chloro-3-methyliminotetrafluorocyclopentene (IX), 0.20 g. (8.5%), m.p. 85–87° (lit.[4] m.p. 88–89°).

Reaction of 1,2,3,3-Tetrachlorotetrafluorocyclopentene (V) with Methylamine.—Using procedure A, V (5.0 g., 0.0175 mole) in 50 ml. of ether gave crude product. Recrystallization from hexane gave colorless crystals of 1-methylamino-2-chloro-3-methyliminotetrafluorocyclopentene (IX), 2.6 g. (63%), m.p. 85–87° (lit.[4] m.p. 88–89°).

Hydrolysis of 1-Methylamino-3-methyliminotrifluorocyclobutene (VI).—Using procedure A, VI was prepared from hexafluorocyclobutene, and the crude product before recrystallization was dissolved in 10 ml. of methanol and 30 ml. of chloroform and chromatographed on an acid-washed alumina column. Elution with 1:1 hexane–ether gave colorless crystals of 3-methylaminotrifluoro-2-cyclobutenone (XII), 9.1 g. (51%), m.p. 109–111°.

Hydrolysis of 1-Methylamino-2-chloro-3-methyliminodifluorocyclobutenone (VII).—Using procedure A, VII was prepared from 1,2-dichlorotetrafluorocyclobutene and methylamine and the crude product was dissolved in warm chloroform and chromatographed on an acid-washed alumina column. Elution with 1:1 hexane–ether gave colorless crystals of 3-methylamino-2-chlorodifluoro-2-cyclobutenone (XIII), 4.9 g. (57%), m.p. 129–130°.

Hydrolysis of 1-Methylamino-3-methyliminopentafluorocyclopentene (VIII) (Procedure B).—A solution of VIII (0.50 g., 0.0023 mole) in 20 ml. of ether was chromatographed on an acid-washed alumina column. The column was allowed to stand overnight before elution. Elution with 1:1 hexane–ether gave colorless crystals of 3-methylaminopentafluoro-2-cyclopentenone (XIV), 0.45 g. (96%), m.p. 120–121°. Recrystallization from chloroform raised the melting point to 120.5–121.0°.

Hydrolysis of 1-Methylamino-2-chloro-3-methyliminotetrafluorocyclopentene (IX).—Using procedure B, IX (0.5 g., 0.0022 mole) gave 3-methylamino-2-chlorotetrafluoro-2-cyclopentenone (XV), 0.46 g. (98%), m.p. 140–141° (lit.[4] m.p. 141–142°).

Hydrolysis of 1-Ethylamino-3-ethyliminopentafluorocyclopentene (X).—Using procedure B, X (0.50 g., 0.0022 mole) gave colorless crystals of 3-ethylaminopentafluoro-2-cyclopentenone (XVI), 0.47 g. (100%), m.p. 84–86°. Recrystallization from hexane–ether raised the melting point to 86–88°.

Hydrolysis of 1-Ethylamino-2-chloro-3-ethyliminotetrafluorocyclopentene (XI).—Using procedure B, XI (0.50 g., 0.0020 mole) gave crude product which was recrystallized from hexane–ether and gave colorless crystals of 3-ethylamino-2-chlorotetrafluoro-2-cyclopentenone (XVII), 0.20 g. (42%), m.p. 104–105°.

Reaction of 1,2-Dichlorohexafluorocyclopentene with Methylamine at 65°.—1,2-Dichlorohexafluorocyclopentene (12.2 g., 0.050 mole), methylamine (10.9 g., 0.35 mole), and 25 ml. of ether were heated at 65° for 7 days in an evacuated, sealed Carius tube. The tube was cooled and opened, and the solution was filtered. Evaporation of the filtrate gave crude product. Recrystallization from hexane gave colorless crystals of 1-methylamino-2-chloro-3-methyliminotetrafluorocyclopentene (IX), 6.0 g. (52%), m.p. 89–90° (lit.[4] m.p. 88–89°).

Reaction of 1-Methylamino-3-methyliminopentafluorocyclopentene (VIII) with Ethylamine (Procedure C).—A solution of VIII (5.0 g., 0.023 mole) and ethylamine (22.5 g., 0.50 mole) in 20 ml. of ether and 5 ml. of methanol was heated in an evacuated, sealed Carius tube at 65° for 4 days. The tube was cooled and opened, the ethylamine hydrofluoride (0.20 g.) was filtered, and the solution was evaporated to give a viscous brown oil. The oil was dissolved in 25 ml. of ether and placed on an acid-washed alumina column. After allowing the column to stand overnight, elution with 1:1 hexane–ether gave colorless crystals of 3-ethylaminopentafluoro-2-cyclopentenone (XVI), 1.50 g. (30%), m.p. 83–86°. Recrystallization from hexane–ether raised the melting point to 86–88°.

Reaction of 1-Methylamino-2-chloro-3-methyliminotetrafluorocyclopentene (IX) with Ethylamine.—Using procedure C, IX (5.8 g., 0.025 mole) and ethylamine (22.5 g., 0.50 mole) in 25 ml. of ether gave, after 4 days at 65°, a viscous yellow oil which failed to crystallize on cooling and seeding. The oil was chromatographed and gave colorless crystals of 3-ethylamino-2-chlorotetrafluoro-2-cyclopentenone (XVII), 3.0 g. (52%), m.p. 104–105°. Further elution gave colorless crystals of 3-methylamino-

(21) D. H. Campbell, Ph.D. Thesis, Purdue University, 1955.

(22) D. H. Campbell proved the structure of V by chemical means. Reaction of V with potassium methoxide gave a dichlorodimethoxytetrafluorocyclopentene which, on treatment with acid, gave the α,β-unsaturated ketone, 2,3-dichlorotetrafluoro-2-cyclopentenone, λ_{max}^{EtOH} 242 mμ (ε 9800).

2-chlorotetrafluoro-2-cyclopentenone (XV), 1.0 g. (18%), m.p. 135–140° (lit.[4] m.p. 141–142°).

Preparation of Hydroxylamine.—In the following reactions hydroxylamine solutions in methanol were prepared by slowly adding a solution of sodium methoxide (59.4 g., 1.1 moles) in 350 ml. of methanol at 0° to a solution of hydroxylamine hydrochloride (83.4 g., 1.2 moles) in 470 ml. of methanol with ice cooling in order to keep the temperature below 30°. After allowing the solution to stand for 5 min. to precipitate the sodium chloride, filtration gave a colorless solution of hydroxylamine (36.3 g., 1.1 moles) in 820 ml. of methanol.

Reaction of Hexafluorocyclobutene (I) with Hydroxylamine (Procedure D).—Hexafluorocyclobutene (15.0 g., 0.097 mole) was introduced slowly through a gas dispersion tube into a stirred solution of hydroxylamine (36.3 g., 1.1 moles) in 820 ml. of methanol at 0° contained in a 1-l. flask fitted with a Dry Ice condenser and drying tube. The reaction was stirred at 0° for 5 hr. and at room temperature for 42 hr. The solution was evaporated to incipient dryness and extracted with eight 250-ml. portions of ether; the ether solutions were evaporated to 25-ml. and chromatographed on a 3.5 × 60 cm. Celite (Johns-Manville, Analytical Filter Aid, acid-washed) column. Elution with 15:85 ether–hexane gave 1,2,3-trioximinodifluorocyclobutane (XVIII) as a cream-white solid, 2.6 g. (72%), m.p. 128° dec. Vacuum drying (50° and 0.1 mm.) for 6 hr. was necessary to remove the last traces of ether. Care must be taken not to use more than 15% ether as an eluent, otherwise the product is obtained as a pasty solid on evaporation of the chromatographic fractions.

Reaction of 1,2-Dichlorotetrafluorocyclobutene (II) with Hydroxylamine.—1,2-Dichlorotetrafluorocyclobutene (II, 15.5 g., 0.080 mole) was added to a stirred solution of hydroxylamine (18.2 g., 0.55 mole) in 420 ml. of methanol and refluxed for 3.5 days. The solution was evaporated and extracted with four 200-ml. portions of THF, the THF was evaporated, and the pasty residue was dissolved in 25 ml. of methanol and 10 ml. of ether. Chromatography as in procedure D gave 1,2,3-trioximinodifluorocyclobutane (XVIII) as a cream-white solid, 10.5 g. (73.5%), m.p. 136° dec.

Preparation of Diazomethane.—A solution of diazomethane (*ca.* 6 g.) in 250 ml. of ether was prepared from N-methyl-N-nitroso-*p*-toluenesulfonamide according to the procedure of de Boer and Backer.[23]

Reaction of 1,2,3-Trioximinodifluorocyclobutane (XVIII) with Diazomethane (Procedure E).—A solution of XVIII (2.7 g., 0.015 mole) in 100 ml. of ether was cooled to 0° and a solution of diazomethane (*ca.* 6 g., 0.14 mole) in 250 ml. of ether was added slowly. The solution was allowed to warm to room temperature and stand for 2.5 hr. Evaporation of the solution and vacuum sublimation (70° and 0.1 mm.) of the brown residue gave crude product. Recrystallization from aqueous methanol and resublimation (50° and 0.1 mm.) gave pale yellow crystals of 1,2,3-tris(methoximino)difluorocyclobutane (XX), 0.15 g. (5%), m.p. 107–108°.

Reaction of Octafluorocyclopentene (III) with Hydroxylamine.—Using procedure D, octafluorocyclopentene (III, 21.2 g., 0.10 mole) was treated with a solution of hydroxylamine (36.3 g., 1.1 moles) in 820 ml. of methanol. After 7 hr. at 0°, 16 hr. at room temperature, and 24 hr. at reflux, additional hydroxylamine (36.3 g., 1.1 moles) in 820 ml. of methanol was added and the solution was refluxed further for 62 hr. The solution was decanted, and the brown residue remaining in the flask was extracted with five 50-ml. portions of ether. The decanted methanolic solution was evaporated, and the orange, pasty residue was extracted with 20 250-ml. portions of ether with stirring. Evaporation of the combined ether extracts gave a viscous reddish orange oil which was dissolved in 10 ml. of methanol and 50 ml. of ether and chromatographed on an acid-washed alumina column. Elution with 1:1 hexane–ether gave 1,2,3-trioximinotetrafluorocyclopentane (XIX) as a cream-white solid, 13.1 g. (57%), m.p. 176° dec. The product was vacuum dried (50° and 0.1 mm.) to remove the last traces of ether.

Reaction of 1,2-Dichlorohexafluorocyclopentene (IV) with Hydroxylamine.—1,2-Dichlorohexafluorocyclopentene (12.2 g., 0.050 mole) was added to a stirred solution of hydroxylamine (36.3 g., 1.1 moles) in 820 ml. of methanol and refluxed for 7 days. The solution was evaporated, and the residue was extracted with 20 150-ml. portions of ether. The ether solution was evaporated, and the resultant yellow paste was digested with three 100-ml. portions of boiling chloroform. The residue was vacuum dried (50° and 0.1 mm.) for 24 hr. and gave 1,2,3-trioximinotetrafluorocyclopentane (XIX) as a cream-yellow solid, 9.0 g. (79%), m.p. 171–172° dec.

Reaction of 1,2,3-Trioximinotetrafluorocyclopentane (XIX) with Diazomethane.—Using procedure E, XIX (3.0 g., 0.013 mole) gave pale yellow crystals of 1,2,3-tris(methoximino)tetrafluorocyclopentane (XXI), 1.9 g. (54%), m.p. 66–68°.

Hydrolysis of 1,2,3-Tris(methoximino)tetrafluorocyclopentane (XXI).—Using the procedure of Eistert,[24] XXI (0.30 g.) was heated with 20 ml. of concentrated hydrochloric acid on a steam cone for 3 hr. until the sample completely dissolved. Cooling the solution and treatment with cold Fehling's solution gave no precipitate.

Reaction of Hexafluorocyclobutene with Hydroxylamine. Kinetic Experiment.—A solution of hydroxylamine (26.4 g., 0.80 mole) in 600 ml. of methanol was purged with nitrogen and cooled to 0°. Hexafluorocyclobutene (30.8 g., 0.20 mole) was introduced over 1 hr. in the vapor phase through a gas dispersion tube and the solution was stirred at 0° for 4 hr. The system was closed to prevent the entrance of air. The resulting red solution had the following ultraviolet spectrum. This and

λ_{max}, mμ	Absorbance	Compound
228	0.68	Trioxime XVIII
240	0.70	Monoxime
290	0.24	Trioxime XVIII

following spectra were run qualitatively in nitrogen-purged methanol. The spectrum did not change over the next 24 hr.

A 50.0-ml. aliquot of the above red reaction mixture was treated with an additional portion of hydroxylamine (13.2 g., 0.40 mole) in 100 ml. of nitrogen-purged methanol at 0°. The solution was thoroughly mixed and divided into two 75-ml. portions, one of which (A) was held at 0° under nitrogen and the other (B) was treated with oxygen introduced through a gas dispersion tube at 0°. The ultraviolet spectra were recorded after 0.5 and 2 hr. of reaction and are tabulated below.

Time, hr.	λ_{max}, mμ	Absorbance	
		Sample A	Sample B
0.5	224	0.84	0.67
	240	0.80	0.62
	290	0.35	0.29
2.0	221	0.76	0.90
	240	0.62	0.71
	290	0.41	0.48

Reaction of 1,2,3,3-Tetrachlorotetrafluorocyclopentene with Hydroxylamine.—1,2,3,3-Tetrachlorotetrafluorocyclopentene (8.0 g., 0.028 mole) and hydroxylamine (3.3 g., 0.11 mole) in 85 ml. of methanol were stirred at room temperature for 5.5 days. Additional hydroxylamine (3.3 g., 0.11 mole) in 85 ml. of methanol was added and the reaction was stirred at 60° for 6 hr. The solution was evaporated and extracted with five 100-ml. portions of ether. The ether solution was evaporated; the residue was dissolved in 25 ml. of carbon tetrachloride and 5 ml. of methanol and chromatographed on an acid-washed alumina column. Elution with 1:1 hexane–ether gave crude product which was vacuum sublimed (55° and 0.2 mm.) to give colorless crystals of 2,3-dichlorotetrafluoro-2-cyclopentenone oxime (XXII), 0.65 g. (9.5%), m.p. 85–86°.

Reaction of 2,3-Dichlorotetrafluoro-2-cyclopentenone Oxime (XXII) with Hydroxylamine.—A solution of XXII (0.65 g., 0.0027 mole) and hydroxylamine (1.8 g., 0.055 mole) in 40 ml. of methanol was refluxed with stirring for 5.5 days. Additional hydroxylamine (1.8 g., 0.055 mole) in 40 ml. of methanol was added and the reaction was refluxed further for 6 days. The solution was evaporated and the residue was extracted with five 75-ml. portions of ether. The ether solution was evaporated to 5 ml. and chromatographed on an acid-washed alumina column. Elution with ether gave 1,2,3-trioximinotetrafluorocyclopentane (XIX) as a yellow pasty solid, 0.15 g. (42%).

Reaction of 1-Methylamino-3-methyliminopentafluorocyclopentene (VIII) with Hydroxylamine. Mild Conditions (Pro-

(23) T. J. deBoer and H. J. Backer, *Rec. trav. chim.*, **73**, 229 (1954).

(24) B. Eisert, R. Mueller, H. Selzer, and E. A. Hackmann, *Chem. Ber.*, **97**, 2469 (1964).

cedure F).—A solution of VIII (2.6 g., 0.012 mole) and hydroxylamine (1.65 g., 0.050 mole) in 50 ml. of methanol was refluxed with stirring for 4 days. The solution was evaporated and the residue was extracted with ten 100-ml. portions of ether. The ether solution was evaporated to 15 ml. and chromatographed on an acid-washed alumina column. Elution with 1:1 hexane–ether gave crude product which was vacuum sublimed (60° and 0.2 mm.) to give colorless crystals of 1-hydroxylamino-3-methyliminopentafluorocyclopentene (XXIII), 1.4 g. (54%), m.p. 108.0–108.5°.

Further elution gave no trioxime XIX.

More Vigorous Conditions.—Using procedure F, VIII (10.8 g., 0.050 mole) and hydroxylamine (36.3 g., 1.1 moles) in 820 ml. of methanol, after 7 days at reflux, gave colorless crystals of 1-hydroxylamino-3-methyliminopentafluorocyclopentene (XXIII), 6.6 g. (62%), m.p. 95–107°. Recrystallization from chloroform and vacuum sublimation (55° and 0.2 mm.) failed to change the melting point.

Further elution gave no trioxime XIX.

Reaction of 1-Methylamino-2-chloro-3-methyliminotetrafluorocyclopentene (IX) with Hydroxylamine. Mild Conditions.—Using procedure F, IX (2.0 g., 0.0083 mole) and hydroxylamine (1.65 g., 0.050 mole) in 50 ml. of methanol, after 4 days at reflux, gave colorless crystals of 1-hydroxylamino-2-chloro-3-methyliminotetrafluorocyclopentene (XXIV), 1.0 g. (50%), m.p. 147–149°.

Further elution gave no trioxime XIX.

More Vigorous Conditions.—Using procedure F, IX (11.5 g., 0.050 mole) and hydroxylamine (36.3 g., 1.1 moles) in 820 ml. of methanol, after 7 days at reflux, gave colorless crystals of 1-hydroxylamino-2-chloro-3-methyliminotetrafluorocyclopentene (XXIV), 4.0 g. (35%), m.p. 140–148°.

Further elution gave 1,2,3-trioximinotetrafluorocyclopentane (XIX) as a cream solid, 0.50 g. (4.4%), m.p. 164° dec.

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Stereoisomeric Enamines. I. Preparation and Characterization[1a,b]

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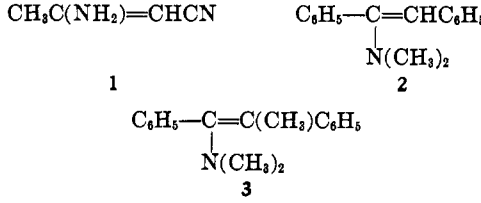
A new approach to the synthesis of stereoisomeric enamines of known configuration is described which takes advantage of the well-documented facility and stereospecificity of the bimolecular β elimination reaction. Treatment of the mesitoate esters of *dl-threo-* and *dl-erythro*-1-(4-morpholino)-1,2-diphenylethanol (**6b** and **8b**, respectively) with potassium *t*-butoxide in dimethyl sulfoxide gave rise to *trans-* and *cis*-1-(4-morpholino)-1,2-diphenylethylene, respectively. Assignment of configuration, relative stability of stereoisomers, and their n.m.r. spectra are discussed.

The general procedures for the preparation of enamines,[2,3] while providing broad scope, fail to incorporate the desirable feature of stereospecificity. The present availability of synthetic methods cannot be considered adequate without the addition of one or more which are stereospecific in character. It is the object of this communication to describe one approach to the fulfillment of this need.

The recorded reports of the synthesis of enamines which can exist as geometric isomers are generally characterized by the absence of a discussion of the stereochemical constitution of the products. It is likely that, where possible, mixtures of stereoisomers are obtained when employing the general procedures[2] whose composition is the result of thermodynamic control. That this is undoubtedly so in the presence of an acid catalyst will be illustrated later. In those cases where the isolation of a single stereoisomer is reported, the synthesis can not be described as stereospecific and the assignment of configuration, if specified, can not be considered rigorous.

The reaction of acetonitrile with sodium is reported[4] to yield either *cis-* or *trans*-β-aminocrotonitrile (**1**), depending on work-up. Assignment of configuration is based on melting point and solubility. Although the authors rule out polymorphic modifications on the basis of thermochemical behavior, it should be noted that the ultraviolet spectra are nearly identical: *cis*, $\lambda_{max}^{acetonitrile}$ 254.5 mμ (ϵ 12,430); *trans*, $\lambda_{max}^{acetonitrile}$ 254.5 mμ (ϵ 13,650).

The *trans* configuration is suggested for enamine **2**, formed in the base-induced dehydrocyanation of 1-(N,N-dimethylamino)-1-cyano-1,2-diphenylethane.[5] Based on the results reported in this paper, that assignment of configuration is suspect. In a similar reaction 1-(N,N-dimethylamino)-1-cyano-2-methyl-1,2-diphenylethane is reported to give rise to a separable mixture of stereoisomeric enamines (**3**); however, assignment of configuration is absent. The authors are careful to point out that a satisfactory elemental analysis was obtained for only one of the two "stereoisomers."



In a study of the preparation of a series of aldehyde enamines (**4**) by the method of Mannich,[2a] Dulou, Elkik, and Veillard[6] assigned the *trans* configuration to the predominant stereoisomer, in what appeared to be

(1) (a) Support of this project by a research grant from Parke, Davis and Co. is gratefully acknowledged. (b) Presented in part before the Division of Organic Chemistry at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964. (c) Parke, Davis Research Fellow 1962–1964.

(2) The two most widely employed procedures are (a) condensation of an aldehyde with a secondary amine in the presence of potassium carbonate [C. Mannich and H. Davidsen, *Ber.*, **69**, 2106 (1936)]; (b) azeotropic removal of water from a solution of a ketone and secondary amine in benzene, frequently in the presence of an acid catalyst. [F. E. Heyl and M. E. Herr, *J. Am. Chem. Soc.*, **75**, 1918 (1953)].

(3) For a brief review of methods of synthesis, see the chapter on enamines, J. Szmuszkovicz, *Advan. Org. Chem.*, **4**, 1 (1963).

(4) J. J. Conn and A. Taurins, *Can. J. Chem.*, **31**, 1211 (1953).

(5) C. R. Hauser, H. M. Taylor, and T. G. Ledford, *J. Am. Chem. Soc.*, **82**, 1786 (1960).

(6) R. Dulou, E. Elkik, and A. Veillard, *Bull. soc. chim. France*, 967 (1960).