this period, 60 ml of water was added and the mixture was steam distilled to give 42.1 g of the crude product, which was fractionated to give 36 g of pure ketone **5** (65% yield), n^{20}_{D} 1.4578, semicarbazone mp 196–198° (lit.[4] 196–197°). The infrared spectrum was superimposable on the spectrum of 3,3,5-trimethylcycloheptanone kindly supplied by Professor Buchi. The mass spectrum showed a parent peak with *m/e* 154, and fragmentation ions with *m/e* 139, 126, 83, 69, 55, 41.

Cyclization of 3,7-Dimethyl-1,6-octadiene (2).—In a three-necked flask fitted with stirrer, thermometer, and reflux condenser was added 44 g of BF_3 etherate to a stirred mixture of 422 g of 3,7-dimethyl-1,6-octadiene and 307 g of formic acid (90%) over a period of 10 min at room temperature (slightly exothermic). The mixture was then heated to 50–60° and stirred at this temperature for 4 hr. Heating was discontinued and the mixture was stirred for another 30 min. An equal volume of water was added and the oil layer was separated. The water layer was extracted twice with benzene. The combined organic layer was washed neutral with sodium bicarbonate solution, and benzene was removed *in vacuo*. After distilling off hydrocarbons the product was fractionated to give 270 g of the formates **6** and **7** (50% conversion). The mixture of formates (**6**, **7**) showed a single peak by glc analysis (20 ft × $^1/_4$ in., SE-30, 5%, packed column). The infrared spectrum (film) showed absorption bands at 5.78 and 8.5 μ. The mass spectrum exhibited a peak at *m/e* 138 (M − 46).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.75; H, 10.89. Found: C, 71.50; H, 11.04.

Hydrolysis of Formates 6 and 7 to Alcohols 8 and 9.—The mixture of formates (11.0 g) was refluxed with 25.0 g of sodium hydroxide and 75 ml of 50% aqueous methanol for 2 hr. After recovering methanol, the crude mixture was acidified with 2% acetic acid and extracted with ether. The ether extract was washed once with sodium carbonate solution and once with water and then dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was distilled to give a mixture of alcohols (**8**, **9**) in 75% yield. Glc analysis indicated two components in an approximate ratio of 4:1. The major peak, isolated by preparative vpc (10% Apeizon, 20 ft × $^1/_4$ in.), was shown to be alcohol **8**: ir (film) hydroxyl band at 2.93 μ; nmr ($CDCl_3$) 0.89, 0.92 [6 H, 2 singlets, $C(CH_3)_2$], 1.08 (3 H, doublet, $CHCH_3$), 1.55 (1 H, broad singlet, for OH), 1.12–1.86 (8 H, multiplet, $-CH_2-$). The mass spectrum showed a parent peak at *m/e* 156.

Anal. Calcd for $C_{10}H_{20}O$: C, 76.95; H, 12.81. Found: C, 76.82; H, 12.77.

Oxidation of Alcohols 8 and 9 to Ketones 10 and 11.—To 52.0 g of mixture of alcohols (**8**, **9**) was added a solution of 40.0 g of chromic acid, 40.0 g of acetic acid, and 40.0 g of water at 25–30° over a period of 1 hr. The reaction mixture was stirred further for 3 hr at 30°. The mixture was then diluted with 60 ml of water and steam distilled to give 43.0 g of the crude product which was distilled to give a mixture of ketones (**10**, **11**), bp 89° (14 mm). Glc analysis using an Apeizon column (10%) 20 ft × $^1/_4$ in. showed two peaks in a ratio of 4:1, respectively. The infrared spectrum (film) of the major compound, obtained by preparative vpc, exhibited a carbonyl band (5.86 μ); nmr (CCl_4) 0.92, 0.95 [6 H, two singlets, $C(CH_3)_2$], 1.12–1.86 (8 H, multiplet, $-CH_2-$), 2.02 [3 H, singlet, $(C{=}O)CH_3$], 2.17–2.55 (1 H, multiplet, $CH(C{=}O)CH_3$]. The mass spectrum showed a peak at *m/e* 154.

Anal. Calcd for $C_{10}H_{18}O$: C, 78.00; H, 11.78. Found: C, 77.82; H, 12.01.

The 2,4-dinitrophenylhydrazone had mp 102–103°.

The infrared spectrum (film) of **11**, the minor component isolated by preparative vpc, exhibited a carbonyl band at 5.84 μ. The nmr spectrum ($CDCl_3$) indicated signals at 0.91, 0.96 [6 H, two singlets, $C(CH_3)_2$], 1.02 (3 H, doublet $CHCH_3$), 2.28 (2 H, AB quartet, J_{AB} = 11.5 Hz, $=OCHCH$), 2.28 (1 H, multiplet, $CHCH_3$), 1.2–1.7 (6 H, multiplet, $-CH_2-$). The 2,4-dinitrophenylhydrazone had mp 136–139° (lit.[3] 137–138°).

Registry No.—**1**, 33515-77-4; **2**, 33515-78-5; *cis*-**3a**, 33511-45-4; *trans*-**3b**, 33511-46-5; **6**, 25225-08-5; **7**, 33515-80-9; **8**, 25225-09-6; **9**, 33515-82-1; **10**, 25304-14-7; **10** 2,4-DNPH, 25412-05-9; **11**, 4436-59-3.

Acknowledgment.—The authors thank Professor G. Stork for helpful discussions with regard to the mechanism of the reaction.

Preparation of Difluoramino-Substituted Vinyl *N*-Fluorimines[1]

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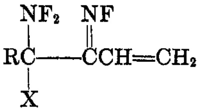
Received November 5, 1970

As part of our synthetic studies on poly(difluoramino) compounds,[2] materials polymerizable by way of the vinyl fluorimine function were prepared. The synthesis and characterization of the difluoramino-substituted vinyl fluorimines Ia–e are described here.[3]

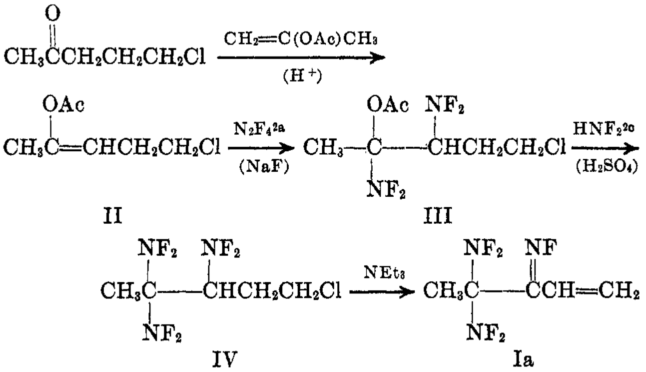


$$RC(NF_2)(X)-C(=NF)CH=CH_2$$

Ia, R = CH_3; X = NF_2
b, R = CH_3; X = Cl
c, R = C_6H_5; X = NF_2
d, R = C_6H_5; X = Cl
e, R = C_6H_5; X = $-OP(O)(OC_2H_5)_2$

The sequence of reactions by which Ia was prepared from 5-chloro-2-pentanone is shown in Scheme I. The

SCHEME I



2-acetoxy-5-chloro-1-pentene accompanying the mixture of *cis*- and *trans*-2-acetoxy-5-chloro-2-pentene (II) produced in the first step could be converted selectively to 5-chloro-2-pentanone and acetic anhydride with an acid catalyst; distillation then removed these contaminants.

The cis and trans isomers of II were identified by proton nmr on the basis of relative shifts of vinyl and acetoxy methyl protons compared with data from the literature for other enol acetate isomers.[4]

The low yields encountered in the conversion of III to IV are undoubtedly due to fragmentation reactions

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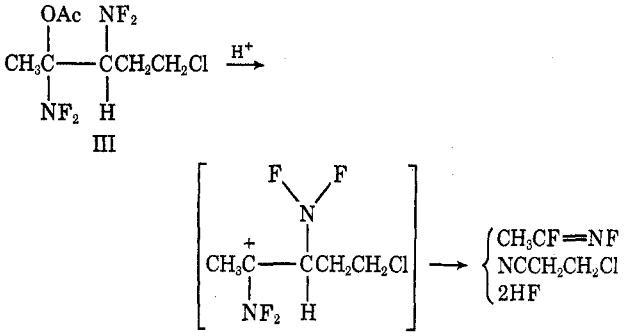
(1) This research was supported by the Advanced Research Projects Agency under U. S. Army Missile Command, Redstone Arsenal, Ala., Contract DA-01-021-11909.

(2) (a) R. C. Petry and J. P. Freeman, *J. Org. Chem.*, **32**, 4034 (1967); (b) W. H. Graham and J. P. Freeman, *ibid.*, **34**, 2589 (1969); (c) J. P. Freeman, R. C. Petry, and T. E. Stevens, *J. Amer. Chem. Soc.*, **91**, 4778 (1969); (d) T. E. Stevens, *J. Org. Chem.*, **34**, 2451 (1969).

(3) The polymerization studies are unpublished results of Dr. Mart Baldwin. In summary, these vinyl fluorimines could not be homopolymerized using AIBN initiator but Va, Vb, and Vd copolymerized with methyl methacrylate and with styrene. A 1:5 Ia–MMA comonomer mixture formed a 1:8 copolymer and a 3:1 Vb–styrene comonomer mixture gave a 1:1 copolymer. Vd copolymerized sluggishly with methyl methacrylate.

(4) H. O. House and V. Kramer, *J. Org. Chem.*, **28**, 3362 (1963).

of the type illustrated; such fragmentations have been observed earlier.[2c] An expected product of this process, β-chloropropionitrile, accompanied IV.

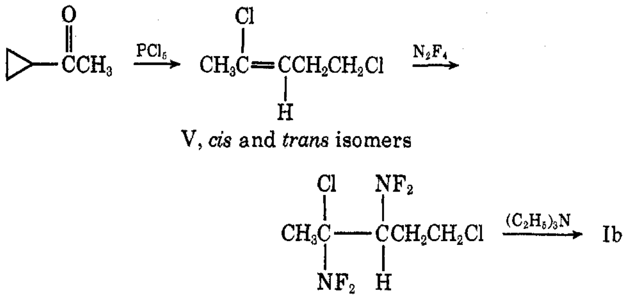


$$\mathrm{CH_3C(OAc)(NF_2)-C(NF_2)(H)CH_2CH_2Cl} \xrightarrow{H^+} \left[\mathrm{CH_3\overset{+}{C}(NF_2)-C(NF_2)(H)CH_2CH_2Cl}\right] \longrightarrow \left\{\begin{array}{l}\mathrm{CH_3CF{=}NF}\\ \mathrm{NCCH_2CH_2Cl}\\ \mathrm{2HF}\end{array}\right.$$

III

Another route devised for the synthesis of Ia is shown in Scheme II. The intermediate 2,3-bis(difluoramino)-2,5-dichloropentane failed to undergo any detectable replacement of chlorine in the 2 position by difluoramine,[5] and consequently this route did not afford any alternative synthesis of Ia. However, the vinyl fluorimine Ib was obtained by dehydrohalogenation of 2,3-bis(difluoramino)-2,5-dichloropentane.

SCHEME II



V, *cis* and *trans* isomers

$$\mathrm{CH_3C(Cl){=}C(H)CH_2CH_2Cl} \xrightarrow{N_2F_4} \mathrm{CH_3C(Cl)(NF_2)-C(NF_2)(H)CH_2CH_2Cl} \xrightarrow{(C_2H_5)_3N} \mathrm{Ib}$$

The preparation of fluorimines Ic, Id, and Ie, carried out by closely related procedures, is outlined in the Experimental Section.

Experimental Section

Melting points and boling points are uncorrected. The ^{19}F nmr spectra were run in CCl_4 or $CDCl_3$ at 40 MHz on a Varian 4300B spectrometer; ϕ values are in parts per million from internal CCl_3F. Proton nmr spectra were recorded on a Varian A-60 spectrometer.

The reaction mixtures and products, including difluoramino compounds, reported below must be considered explosive hazards. Adequate shielding must be employed at all times. Accurate elemental analyses are difficult to obtain on polydifluoramino compounds; many samples, including Ia, have exploded in the combustion furnace. Thus, nmr spectral data was used extensively for characterization purposes.

2-Acetoxy-5-chloro-2-pentene.—A mixture of 100 g (1.0 mol) of isopropenyl acetate, 60 g (0.5 mol) of 5-chloro-2-pentanone, and 1.4 g (0.0074 mol) of *p*-toluenesulfonic acid was heated under a distilling column removing 39 ml (*ca.* 0.5 mol) of acetone during 5.5 hr (some acetyl chloride was present in the acetone). The mixture was cooled, treated with 2 g of anhydrous sodium acetate, stirred for 0.5 hr, filtered, and distilled rapidly under reduced pressure without fractionating, giving 33 g of volatiles (condensed in a CO_2 trap), 67 g of crude product, and 7 g of residue. The volatiles consisted mainly of isopropenyl acetate with a little acetone. The crude product fraction, by glc,[6] consisted of isopropenyl acetate (1.3%), acetic anhydride (4%), 5-chloro-2-pentanone (22%), *trans*[7]-2-acetoxy-5-chloro-2-pentene (34%), *cis*-2-acetoxy-5-chloro-2-pentene (11%), and 2-acetoxy-5-chloro-1-pentene (28%).

Separation of the three isomeric acetoxychloropentenes from one another could not be effected by fractional distillation. However, the 2-acetoxy-5-chloro-1-pentene was selectively destroyed (converted to ketone, pentene-2 isomers, and acetic anhydride) by stirring for several hours over 10–20% by weight of Amberlyst[8]-15 or additional toluenesulfonic acid. This treatment was applied to crude reaction mixture, to distilled crude mixtures (as above), and to distilled mixtures of product isomers from which ketone had been removed in forefractions and succeeded in all cases.

For example, to 88.5 g of a crude, distilled reaction product mixture which was stirred at room temperature was added three 5-g portions of Amberlyst-15 resin over 24 hr. At the end of this time, glc assay of the mixture showed that all of the pentene-1 component had disappeared. The mixture was distilled through a 36-in. spinning-band column, collecting a forerun which was principally ketone, bp 34° (3 mm). When this fraction was finished, the pot residue was cooled, removed, and distilled rapidly through a short-path apparatus, collecting 23.4 g of mixed *trans*- and *cis*-2-acetoxy-5-chloro-2-pentene isomers, bp 50° (3 mm).

Anal. Calcd for $C_7H_{11}O_2Cl$: C, 51.69; H, 6.77. Found: C, 51.59; H, 6.99.

The isomers were identified from proton nmr spectra of glc fractions trapped separately. These data are summarized in Table I.

TABLE I

CCl_4 soln	trans (AcO–H), δ	cis (AcO–H), δ
5-CH_2Cl	t, 3.41	3.5
4-CH_2	q, 2.3	2.45
3-=CH	t, 5.02	5.1
2-OAc	s, 2.08	2.01
1-CH_3	s, 1.85	1.85

2,3-Bis(difluoramino)-2-acetoxy-5-chloropentane (III).—A solution of 18 g (0.111 mol) of 2-acetoxy-5-chloro-2-pentene in 25 ml of CCl_4 containing 3.5 g of NaF was stirred in a 90-ml Fisher-Porter tube under 200–300 psi of N_2F_4; the temperature of 115° was maintained for 5 hr. The mixture was allowed to cool, the apparatus was vented and flushed with nitrogen, and the product was isolated from the filtrate after evaporation of solvent. This material was used directly in the next step. A sample of 2,3-bis(difluoramino)-2-acetoxy-5-chloropentane was isolated from an earlier run, bp 50° (0.1 mm).

Anal. Calcd for $C_7H_{11}N_2O_2ClF_4$: C, 31.52; H, 4.14; N, 10.51; F, 28.52. Found: C, 31.82; H, 4.27; N, 11.99; F, 27.2.

The proton and fluorine nmr spectra were attributable to an isomer mixture. The proton spectrum had two $CH_3(C{=}O)O$ singlets at δ 2.12 and 2.15. The ^{19}F spectrum had two tertiary $-NF_2$ singlets, nearly superimposed at ϕ -23.2. The secondary $-NF_2$ group appeared as a superposition of two AB quartets near -1800 Hz.

3,4,4-Tris(difluoramino)-1-chloropentane (IV).—The solution of 18 g (0.111 mol) of *trans*-2-acetoxy-5-chloro-2-pentene in 25 ml of CCl_4, saturated with N_2F_4 as above, was added dropwise onto 0.425 mol of HNF_2 refluxing from a CO_2 cold finger over a stirred mixture of 10 ml of 30% fuming H_2SO_4 and 7 ml of CCl_4 at -10 to 16°. The mixture was kept at 14–16° for 90 min after the addition. Layers were separated; the acid layer was quenched and extracted with CCl_4; and the extracts were combined, washed with water, $NaHCO_3$ solution, and water, and dried with $MgSO_4$. Solvent was distilled at atmospheric pressure and the residue at 2.7–2.9 mm to give a β-chloropropionitrile mixture comprising 1.5 g, bp 39–42°, 0.6 g, bp 42–45°, and 6.2 g, bp 45° (IV).

Anal. Calcd for $C_5H_8ClN_3F_6$: C, 23.12; H, 3.08; N, 16.18; Cl, 13.68; F, 43.93. Found: C, 23.34; H, 3.09; N, 16.46; Cl, 13.2; F, 45.0.

The ^{19}F nmr spectrum had a geminal NF_2 singlet at ϕ -28.5; the secondary $-NF_2$ group was an AB quartet near -1740 Hz.

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(5) Conversion of $\mathrm{Cl\overset{|}{C}NF_2}$ to $\mathrm{NF_2\overset{|}{C}NF_2}$ has been reported by K. Baum, *J. Org. Chem.*, **34**, 2046 (1969), and by K. Johnson, Rohm and Haas Co., Redstone Research Laboratories, unpublished results.

(6) Determined by using a 10-ft Carbowax 20M on firebrick 60–80 column.

(7) The acetoxy and hydrogen atom trans.

(8) Trademark of Rohm and Haas Co., Philadelphia, Pa.

4,4-Bis(difluoramino)-3-fluorimino-1-pentene (Ia).—A solution of 6.7 g (0.026 mol) of the tris(NF_2)chloropentane IV in 40 ml of CH_2Cl_2 was stirred in an ice bath while a solution of 5.2 g (0.052 mol) of triethylamine in 5 ml of CH_2Cl_2 was added dropwise holding the temperature at 5–7°. The addition required 40 min, after which stirring at 0° was continued for 30 min and, after reaching room temperature, for 1 hr. The mixture (which had not darkened) was filtered and the CH_2Cl_2 solution was extracted with 5% aqueous HCl and two portions of water and dried with $MgSO_4$. Solvent was distilled off through a Holtzman column at atmospheric pressure and the product at 50° (50 mm). The yield was 2.2 g, 42% of theoretical.

Anal. Calcd for $C_5H_6N_3F_5$: C, 29.56; H, 2.96; N, 20.69; F, 46.8. Found: C, 29.17; H, 3.66; N, 21.42; F, 48.8.

2,5-Dichloropentene-2.—A suspension of 118 g (0.565 mol) of PCl_5 in CH_2Cl_2 was stirred in a three-neck flask equipped with a condenser and drying tube while 48 g (0.565 mol) of methyl cyclopropyl ketone was added to it slowly dropwise controlling the temperature at 15–18° by external cooling. When the suspended PCl_5 had all reacted (clear solution) the condenser was replaced by a Vigreux column and solvent was distilled until the pot temperature reached 95°. The pot was cooled, the pressure was reduced to 90–100 mm, and $POCl_3$ was distilled at 38–52° head temperature. The pot residue was cooled again, poured into ice and water, and stirred for 1–2 hr. One volume of CH_2Cl_2 was added, and the lower layer was separated, washed with water and $NaHCO_3$ solution, and dried with $MgSO_4$. Since the dried solution still gave an acid reaction when shaken with water, some anhydrous Na_2CO_3 was added and the solution was stirred for 2 hr. Solids were filtered, solvent was evaporated, and the product was distilled away from the residue at 48–52° (14 mm), giving 29 g of distillate. This proved to be a mixture of *cis*- (Me–H) and *trans*- (Me–H) 2,5-dichloropentene-2, which, for synthetic purposes, was used directly. It was separated by fractional distillation through a 24-in. spinning band column collecting pure fractions (by glc assay): (1) 14.4 g, bp 44° (10.0 mm), $n^{20}\mathrm{D}$ 1.4681; (2) 2.8 g, bp 54° (9.8 mm), $n^{20}\mathrm{D}$ 1.4744.

Anal. Calcd for $C_5H_8Cl_2$: C, 43.17; H, 5.76. Found: (1) C, 42.59; H, 5.93; (2) C, 43.52; H, 6.11.

2,3-Bis(difluoramino)-2,5-dichloropentane.—A solution of 13.5 g (0.1 mol) of 2,5-dichloropentene-2 ($n^{20}\mathrm{D}$ 1.4681) in 30 ml of CH_2Cl_2 was saturated with N_2F_4 at 95° (300 psi) during 7 hr and was left under pressure overnight. The product solution was evaporated and the residue was distilled through a Holtzman column, collecting 19.1 g of distillate in fractions, bp 40–47° (<1 mm), $n^{20}\mathrm{D}$ 1.4293–1.4297. The ^{19}F nmr spectrum had peaks at ϕ −33.4 ($ClCNF_2$) and two NF_2 AB quartets near −1760 Hz.

Reaction of 2,3-Bis(difluoramino)-2,5-dichloropentane with HNF_2–H_2SO_4.—A solution of 11.3 g of the above pentane in 23 ml of CH_2Cl_2 was added dropwise onto 0.4 mol of HNF_2 refluxing from a CO_2 cold finger condenser over a stirred mixture of 10 ml of 30% fuming H_2SO_4 and 7 ml of CH_2Cl_2. The addition was finished in 10 min at −10 to 21°. Stirring was continued for 5 hr at 10°. Work-up of the product resulted in recovery of 63% of the bisdifluoramino dichloropentane, identified by its ^{19}F nmr spectrum. No evidence of the presence of any 3,4,4-tris(difluoramino)-1-chloropentane was detected.

4-Difluoramino-4-chloro-3-fluoriminopentene-1 (Ib).—A solution of 4.1 g (0.041 mol) of triethylamine in 5 ml of CH_2Cl_2 was added dropwise to a stirred solution of 5 g (0.02 mol) of 2,3-bis-(difluoramino)-2,5-dichloropentane in 40 ml of CH_2Cl_2 at 0°, controlling the exotherm by external cooling. The mixture was stirred at 0° for 30 min after addition and at room temperature for another hour. Solids were filtered and the filtrate was washed with cold 5% aqueous HCl and water and dried. Solvent was distilled at atmospheric pressure and the residue was distilled under reduced pressure, giving a forerun (0.15 g) and 2.1 g of product, bp 55° (50 mm).

Anal. Calcd for $C_5H_6N_2F_3Cl$: C, 32.17; H, 3.22; N, 15.01; F, 30.56. Found: C, 32.13; H, 3.43; N, 15.88; F, 30.9.

The ^{19}F nmr spectrum had peaks at ϕ −21.1 (C═NF) and an AB quartet near −4500 Hz.

Preparation of 1-Phenyl-1-chloro-1-difluoramino-2-fluorimino-3-butene (Id).—1,4-Dichloro-1-phenyl-1-butene, bp 103° (0.8 mm), prepared from phosphorus pentachloride and γ-chlorobutyrophenone, was exposed to tetrafluorohydrazine in the usual fashion (Freon 113–methylene chloride solvent).[2a] The crude adduct from 6.0 g (30 mmol) of olefin was dissolved in 50 ml of *tert*-butyl alcohol and at 20° 50 ml of 1.10 *N* potassium *tert*-butoxide in *tert*-butyl alcohol was added. After 30 min the mixture was poured into H_2O, and the organic product was extracted into methylene chloride. The residue was chromatogaphed on silica gel to give, in the 10:1 pentane–methylene chloride eluate, 5.5 g of a mixture of the desired product and material that had not been dehydrochlorinated. This was taken up in *tert*-butyl alcohol (25 ml) and 7 ml of 1.10 N potassium *tert*-butoxide was added. The usual work-up of this reaction (chromatography on silica gel) gave 1-phenyl-1-chloro-1-difluoramino-2-fluorimino-3-butene, 2.35 g, a colorless liquid.

Anal. Calcd for $C_{10}H_8ClF_3N_2$: C, 48.30; H, 3.24; N, 11.27; F, 23.0. Found: C, 48.12; H, 3.51; N, 11.16; F, 21.7.

The ^{19}F nmr spectrum had peaks at ϕ −26.4 (C═NF) and an AB quartet with ϕ_A near −43.9 and ϕ_B near −37.2 (J_{FF} = 552 Hz).

Preparation of 1-Phenyl-1,1-bis(difluoramino)-2-fluorimino-3-butene (Ic).—1-Phenyl-1,1,2-tris(difluoramino)-4-chlorobutane was prepared in the usual way[2c] from 1-phenyl-1-(diethylphosphoryloxy)-1,2-bis(difluoramino)-4-chlorobutane and was isolated as a colorless liquid.

Anal. Calcd for $C_{10}H_{10}ClN_3F_6$: C, 37.34; H, 3.13; N, 13.06; F, 35.4. Found: C, 37.32; H, 3.18; N, 13.18; F, 34.5.

The ^{19}F nmr spectrum exhibited $C(NF_2)_2$ at ϕ −26.5 and $HCNF_2$ as a quartet of doublets, center members at −2110 and −1604 Hz.

Dehydrofluorination of the trisdifluoramino chlorobutane (3.50 g) in 25 ml of methanol and 10 ml of methylene chloride at 0° with 7.8 ml of 1.40 *N* sodium methoxide in methanol gave 3.2 g of product that had undergone some dehydrochlorination (proton nmr). Therefore, the 3.2 g of product was dehydrochlorinated in 25 ml of *tert*-butyl alcohol with 10 ml of 1.02 *N* potassium *tert*-butoxide in *tert*-butyl alcohol. The product, 2.9 g, was chromatographed on silica gel. 1-Phenyl-1,1-bis(difluoramino)-2-fluorimino-3-butene was obtained in the pentane–methylene chloride (10:1) eluate, 2.16 g, a colorless liquid.

Anal. Calcd for $C_{10}H_8N_3F_5$: C, 45.29; H, 3.04; N, 15.85; F, 35.8. Found: C, 44.30; H, 3.62; N, 16.18; F, 34.6.

The ^{19}F nmr spectrum showed $C(NF_2)_2$ at ϕ −31.9 and >C═NF at ϕ −37.7.

Reaction of 1-Phenyl-1,2-bis(difluoramino)-1-(*O,O*-diethylphosphoryloxy)-4-chlorobutane and Potassium *tert*-Butoxide.—A solution of 53 g (125 mmol) of the above N_2F_4 adduct[2c] in 100 ml of methylene chloride and 150 ml of *tert*-butyl alcohol was stirred at 10° while 116 ml of 1.08 *N* potassium *tert*-butoxide in *tert*-butyl alcohol was added dropwise. The solution was neutral at this time, and a ^{19}F nmr spectrum of a portion of the organic product indicated that a considerable portion of unreacted starting material was still present. Addition of the *tert*-butoxide solution was continued until the solution remained basic; an additional 151 ml of the standard base was required. The reaction mixture was processed as usual. The solid product was recrystallized from hexane–chloroform to give 1-phenyl-1-difluoramino-1-(*O,O*-diethylphosphoryloxy)-2-fluorimino-3-butene (24 g), mp 64–66°.

Anal. Calcd for $C_{14}H_{18}N_2O_4PF_3$: C, 45.91; H, 4.95; N, 7.65. Found: C, 45.61; H, 5.27; N, 7.45.

The ^{19}F nmr spectrum had peaks for –C═NF at ϕ −27.6 and for –CNF_2, AB quartet with ϕ_A near −31 and ϕ_B near −27.2, J_{FF} = 552 Hz.

Registry No.—Ia, 33364-51-1; Ib, 33364-52-2; Ic, 33364-53-3; Id, 33364-54-4; *cis*-II, 33364-55-5; *trans*-II, 33364-56-6; III, 33364-57-7; IV, 33364-58-8; *cis*-V, 5680-46-6; *trans*-V, 5680-47-7; 2,3-bis(difluoramino)-2,5-dichloropentane, 33364-60-2; 1-phenyl-1-difluoramino-1-(*O,O*-diethylphosphoryloxy)-2-fluorimino-3-butene, 33364-61-3.