bath and treated with 3.2 ml of 3 *N* NaOH and 3.2 ml of 30% H_2O_2. After 2 hr at room temperature, the reaction mixture was poured into 500 ml of H_2O, the aqueous solution extracted with ether, and the ether extract washed with water and dried over Na_2SO_4. The infrared spectrum of the residue remaining after removal of solvent and drying agent showed that very little of the aldehyde **37** had been formed and that only traces of starting material remained. Attempts to isolate the aldehyde by glpc were unsuccessful. The crude product obtained above was added to a THF solution of the ylide prepared from 2.06 g of triphenylisopropylphosphonium bromide and butyllithium. After 24 hr at room temperature the mixture was poured into 500 ml of H_2O and the aqueous phase extracted with pentane. The pentane solution was washed with water, dried over $MgSO_4$, and filtered and the solvent removed *in vacuo*. The residue was adsorbed on 30 g of alumina. Elution with pentane gave 21.0 mg of crude hydrocarbons, containing some starting acetylenic olefin and the desired (−)-α-*cis*-bergamotene. Purification by glpc gave 8.5 mg of pure material, $\lambda_{max}^{CCl_4}$ 6.05, mol wt 204 (mass spectroscopy), $[\alpha]_{5461}$ −39.4° (*c* 0.48, $CHCl_3$), and nmr signals at τ 8.82 (1 H, d, *J* = 8 Hz), 8.73 (3 H, s), 8.43 (3 H, s), 8.36 (3 H, s), 8.32 (3 H, d, *J* = 2 Hz), 7.82 (5 H), 4.99 (1 H, brd t, *J* = 7 Hz), and 4.85 (1 H, m). The infrared and nmr spectra of this material were identical with those of a sample isolated from oil of opoponax,[8] which showed $[\alpha]_{5461}$ −45° (*c* 0.038, $CHCl_3$).

Acknowledgment. The authors wish to acknowledge the excellent technical assistance of Mr. Kenneth M. Pieper.

The Synthesis of 1,2,2-Tris(difluoramino)alkanes[1a]

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Abstract: Enol esters are converted to 1,2,2-tris(difluoramino)alkanes when treated successively with tetrafluorohydrazine and difluoramine–sulfuric acid. Some of the limitations of this reaction are described. The tris(difluoramino)alkanes are stable compounds; their chemistry resembles that of olefin–tetrafluorohydrazine adducts.

The synthesis of poly(difluoramino) compounds of specific configurations presents some special problems. Essentially, there are two general methods available. The addition of tetrafluorohydrazine to an olefin double bond[2] and the conversion of carbonyl groups[3] or their equivalent[4] to *gem*-difluoramines using difluoramine in strong acids. Attempts to combine these reactions with α,β-unsaturated ketones have been frustrated by the instability of the olefin–N_2F_4 adduct[2] and by the tendency of difluoramine to add to the olefinic double bond.[4] For example, difluoramine reacts with methyl vinyl ketone in the presence of sulfuric acid to yield 1,3,3-tris(difluoramino)butane.[3,5] The α-alkyl-α-difluoraminocarbonyl compounds encountered in this study were unstable in strong acid; fragmentation, as discussed below, was observed.

$$CH_3\overset{O}{\overset{\|}{C}}CH{=}CH_2 \xrightarrow[H_2SO_4]{HNF_2} CH_3C(NF_2)_2CH_2CH_2NF_2$$

In searching for useful intermediates for combining the N_2F_4 and HNF_2 reactions, it appeared that enol derivatives would offer a useful and potentially convenient route for the conversion of a ketone function to a tris(difluoramino) function. Enol esters react readily with tetrafluorohydrazine[2] and it has now been established that the resulting adducts are cleaved by difluoramine in strong acids to yield the desired derivatives.

$$\diagdown C{=}C(\mathrm{OR})\diagup + N_2F_4 \longrightarrow \diagdown \underset{NF_2}{C}-\underset{NF_2}{C}(\mathrm{OR})\diagup + HNF_2 \xrightarrow{H^+} \diagdown \underset{NF_2}{C}-\underset{NF_2}{C}(NF_2)\diagup$$

Results

Both enol phosphates and enol acetates have been employed in this sequence. Both have virtues and drawbacks. When the requisite α-halo ketone is available, the enol phosphate is useful because the double bond is located unequivocally between the carbonyl carbon and carbon originally bearing halogen. However, in many instances it is not convenient to prepare and purify the desired monohalo ketone. Enol acetates are easier to prepare, but unless a symmetrical ketone is employed mixtures result. Decision in individual instances must be made on the basis of these considerations.

The reaction of the α,β-bis(difluoramino)alkyl acetates or phosphates with difluoramine in fuming sulfuric acid or fluorosulfonic acid was very sensitive to the structure of the ester and to the reaction conditions. It was generally found necessary to carry out these reactions in the presence of methylene chloride to extract the tris(difluoramine) from the reaction zone.

Some of the representative tris(difluoramines) prepared are listed in Table I. In general, the intermediate N_2F_4 adducts were not purified but were used directly. In all cases they were characterized by nmr analyses. The low molecular weight tris(difluoramines) are extremely sensitive compounds, and explode readily when initiated by friction or impact. Extreme care was necessary in their handling. Great difficulty was

(1) (a) This research was carried out under Army Ordnance Contract No. DA-01-021-ORD-11909. (b) Deceased. (c) Address inquiries to this author.

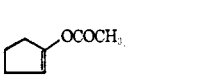
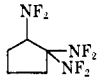
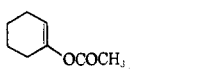
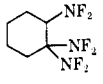
(2) R. C. Petry and J. P. Freeman, *J. Org. Chem.*, **32**, 4034 (1967).

(3) K. Baum, *J. Am. Chem. Soc.*, **90**, 7083 (1968).

(4) W. H. Graham and J. P. Freeman, *J. Org. Chem.*, in press.

(5) Addition to HNF_2 to α,β-unsaturated ketones[3] appears to be a general route to 1,3,3-tris(difluoramino)alkanes. Cyclohexenone and cyclopentenone were converted to 1,1,3-tris(difluoramino)cyclohexane and 1,1,3-tris(difluoramino)cyclopentane, respectively; an example is given in the Experimental Section.

Table I. Preparation of 1,2,2-Tris(difluoramines)

Olefin	Product	Calcd, % C	H	N	F	Found, % C	H	N	F	F^{19} nmr resonance[a]
$CH_2=CHOCOCH_3$	$NF_2CH_2CH(NF_2)_2$									−2232 (CH_2NF_2), −1480 [$CH(NF_2)_2$]
$CH_3C(OCOCH_3)=CH_2$	$CH_3C(NF_2)_2CH_2NF_2$									−2488 [CH_2NF_2], −1124 [$C(NF_2)_2$]
$CH_3C(OP(=O)(OC_2H_5)_2)=CHCH_3$	$CH_3C(NF_2)_2CH(NF_2)CH_3$	22.76	3.34	19.90	54.00	20.97	3.83	20.64	53.7	−1128 [$C(NF_2)_2$], −1954 ($CHNF_2$), −1227 (J_{FF} = 595 cps)[b]
$C_6H_5C(OP(=O)(OC_2H_5)_2)=CHCH_2CH_2Cl$	$C_6H_5(NF_2)_2CH(NF_2)CH_2CH_2Cl$	37.34	3.13	13.06	35.44	37.3	3.18	13.14	34.5	1040 [$C(NF_2)_2$][d], −2324 ($CHNF_2$), −1364 (J = 588 cps)[b]
$CH_2=C(OP(=O)(OC_2H_5)_2)-CH_2Cl$	$NF_2CH_2C(NF_2)_2CH_2Cl$									−1216 [$C(NF_2)_2$], −2104 ($CHNF_2$)[c] −1992
$CH_3CH_2C(OP(=O)(OC_2H_5)_2)=CHCH_3$	$CH_3CH_2C(NF_2)_2CH(NF_2)CH_3$	26.67	4.03	18.67		27.29	4.21	19.13		−1108 [$C(NF_2)_2$], −2004 ($CHNF_2$), −1324 (J_{FF} = 595 cps)[b]
$C_6H_5CH=CCH_3$ (OCOCH$_3$)	$C_6H_5CH(NF_2)C(NF_2)_2CH_3$	39.57	3.22	15.38		40.84	3.55	16.09		−2092 (CH–NF_2)[b] −1372 (J_{FF} = 600 cps)[b]
$C_6H_5C(OCOCH_3)=CHCH_3$	$C_6H_5C(NF_2)_2CH(NF_2)CH_3$	39.57	3.22	15.38	41.7	39.42	3.47	16.27	42.9	−960 [$C(NF_2)_2$]
		26.91	3.16	18.83	51.09	26.68	3.54	18.45	51.00	−1348 [$C(NF_2)_2$], −2048 ($CHNF_2$), −2272 (J = 588 cps)
		30.39	3.83	17.72	48.1	30.73	4.44	17.89	46.8	−1000 [$C(NF_2)_2$], −2187 ($CHNF_2$), −1508 (J_{FF} = 600 cps)[b]

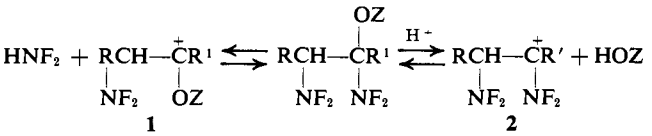
[a] At 40 Mc from Freon 11 internal standard in cps. [b] AB portion of ABX spectrum. [c] Only the center lines of the AB portion of an ABX spectrum were visible. [d] Center line of an AA'BB'X spectrum.

encountered in their analysis by combustion. Since nmr analysis proved to be absolutely reliable, it was used exclusively for characterization of some compounds.

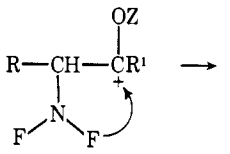
Discussion

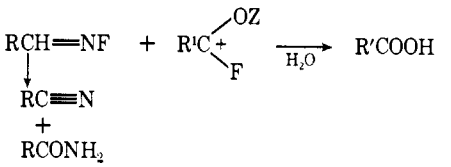
In general it was found that the addition of tetrafluorohydrazine to enol esters proceeded smoothly as previously outlined.[2] The presence of the phosphate linkage caused no special problems.

The cleavage of the enol ester–N_2F_4 adducts proved to be quite a variable, almost capricious, reaction. The basis for the difluoramine cleavage reaction is the acid-catalyzed ionization of the organic derivatives to a carbonium ion. Competing with the removal of the ester function, however, is the loss of difluoramine. Undoubtedly ion **1** is more stable. In fact, in many instances it appears that this ion is formed exclusively, and then decomposes in acid solution by a fragmentation reaction which may be generalized as shown.[6]



1 **2**

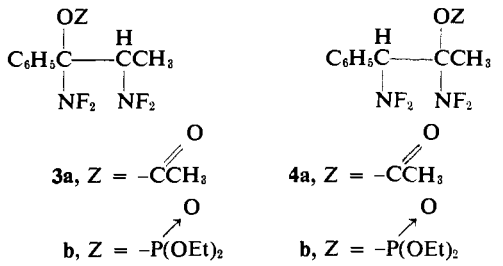




Both 3-(diethylphosphato)- and 3-acetoxy-2,3-bis(difluoramino)pentane evolved difluoramine when exposed to sulfuric acid; no 2,3,3-tris(difluoramino)pentane was produced under those conditions when the reaction was carried out in the presence of difluoramine. Instead, propionic acid was obtained after dilution and extraction of the acid layer. However, under the identical conditions, 2-(diethylphosphato)-2,3-bis(difluoramino)butane and 2-acetoxy-1,2-bis(difluoramino)pro-

(6) The reaction of all these esters with sulfuric acid was strongly exothermic, and undoubtedly the heat of solution contributed to the decomposition. It might have been anticipated that ion **1** would be unstable since other compounds in which the difluoramino group is adjacent to an atom with available bonding orbitals undergo cleavage with migration of fluorine to the electron-deficient atom.[2]

pane were converted to the corresponding tris(difluoramines).[7] The four substituted 1-phenylpropanes **3a**, **3b**, **4a**, and **4b**, all fragmented in sulfuric acid solution.

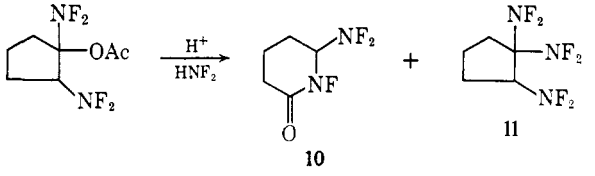


From both **3a** and **3b**, difluoramine and benzoic acid were the products isolated; from **4a** and **4b**, benzonitrile and benzamide were produced.

The facile loss of HNF_2 from these compounds in strong acids may be an indication of considerable strain which is relieved upon a change from sp^3 to sp^2 hybridization. Undoubtedly this kind of ionization occurs with all enol ester–N_2F_4 adducts, but is reversible only in the less crowded materials. Thus when R and R^1 are hydrogen or methyl, ion **1** can be converted to ion **2**. When R and R^1 are larger than methyl, ion **1** is reluctant to return to a tetrahedral configuration and indeed the carbonium ion center is probably highly shielded by the appendant groups. Such steric acceleration of ion formation has been proposed for highly hindered halides.[8]

These problems with decomposition were largely circumvented by carrying out the reactions in the presence of methylene chloride. This solvent appeared to function in two ways. First, it acted as a heat sink and moderated the exothermic reaction which occurred between the ester and acid upon warming from −130° to room temperature. Second, it functioned to extract the tris(difluoramine) from the acid. It was found that a tris(difluoramine) added to sulfuric acid led to evolution of difluoramine.

The preparation of 1,1,2-tris(difluoramino)cyclopentane (**11**) was hindered by the tendency of 1-acetoxy-1,2-bis(difluoramino)cyclopentane (**9**) to rearrange to 3-difluoramino-2-fluoro-2-azacyclohexanone (**10**).[9] Only



with the use of a large excess (five- to tenfold) of difluoramine was the preparation of **11** reasonably successful. The azacyclohexanone **10** always formed to some extent; in small-scale vacuum-line runs **10** was the only organic product isolated.[10]

Much higher yields (70% *vs.* 30%) of **10** were obtained from **9** when added difluoramine was present. Whether the added difluoramine suppressed destruction of **9** *via* the α-acetoxycarbonium ion related to **1**, or whether **10** arose from an α-difluoramino ketone such as **12**, in the manner indicated, is not known.[11]

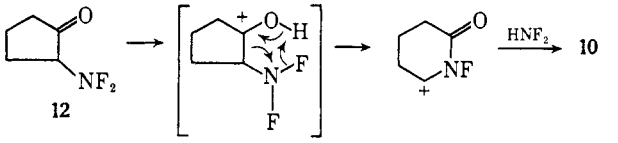
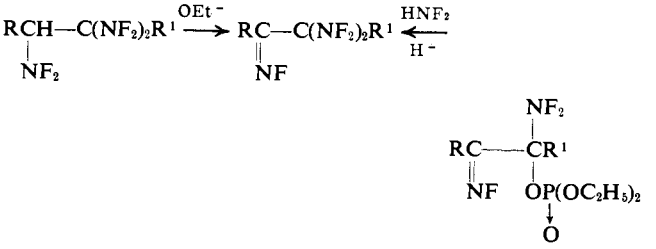


Table II summarizes the results of several preparations of tris(difluoramino)alkanes conducted in the presence of refluxing difluoramine. Other examples of vacuum-line techniques are given in the Experimental Section.

The last two examples in Table II show the direct preparation of α,α-bis(difluoramino)fluorimines from the dehydrofluorinated N_2F_4–enol phosphate adduct. Since the synthetic utility of the α,α-bis(difluoramino)-fluorimines was the main incentive for this work, these conversions were of considerable interest. The enol acetate adducts could not be dehydrofluorinated with-



out decomposition.[12] However, this route to bis(difluoramino)fluorimines was of practical use only when the phosphate group was adjacent to an aromatic ring. Apparently, loss of the phosphate moiety to give the requisite carbonium ion was only then appreciably faster than competing side reactions such as Beckmann cleavage or rearrangement[13] of the fluorimine function.

Experimental Section

Safety Precautions. It should always be kept in mind that difluoramine is explosive in the condensed state. All transfers involving condensation of this material should be carried out behind adequate shields. Since it is known that air, organic materials, and NF gases constitute a particularly explosive combination, all reaction mixtures should be thoroughly deaerated before admitting the HNF_2. Most of the tris(difluoramines) were sensitive to initiation by friction and/or impact and should be handled in small quantities and with adequate shielding.

Preparation of 1,2,2-Tris(difluoramino)propane. The isopropenyl acetate–N_2F_4 adduct (0.8 g, 0.004 mole) was added to a mixture of 1.25 ml of 30% fuming sulfuric acid at −80°. This mix-

(7) The capriciousness of the reaction can be illustrated by the behavior of 2-(diethylphosphato)-2,3-bis(difluoramino)butane. Although the conversion of this material to 2,2,3-tris(difluoramino)butane proceeded readily in small-scale (5–10-mmole) runs, attempts to scale the reaction to the 100–200-mmole size gave only cleavage. Violent explosions were encountered in sealed pressure reactors. However, the use of methylene chloride as solvent allowed the reaction to proceed reproducibly.

(8) H. C. Brown and H. L. Berneis, *J. Am. Chem. Soc.*, 75, 10 (1953), and preceding papers.

(9) A rather detailed report of this rearrangement has appeared: T. E. Stevens and W. H. Graham, *ibid.*, 89, 182 (1967).

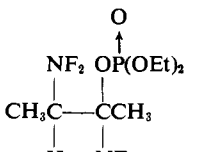
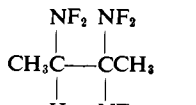
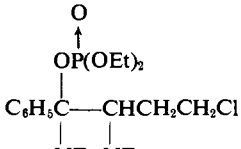
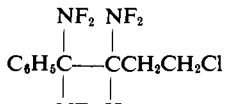
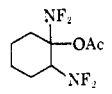
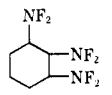
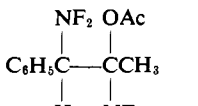
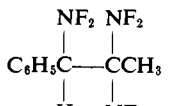
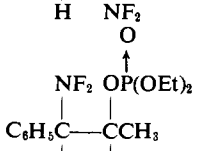
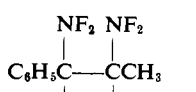
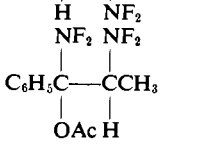
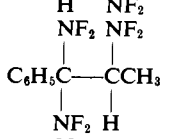
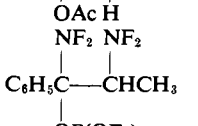
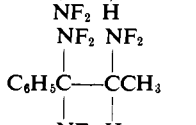
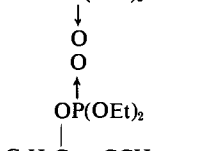
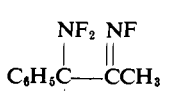
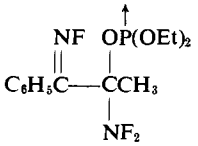
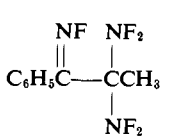
(10) The *cis* and *trans* isomers of **9** were separated (vpc), and each was treated with HNF_2–H_2SO_4 to see if one isomer would rearrange and the other would convert to **11**. Ketone **10** was isolated from each isomer, however.

(11) At low temperature (−40°), sulfuric acid converted some 1-acetoxy-1,2-bis(difluoramino)alkanes to α-difluoramino ketones. These ketones fragmented readily (to nitrile and acid fluoride) and could not be isolated in a pure state. There was no sign, however, that **12** formed from **9**.

(12) The one-step synthesis of α-acetoxy-α-difluoraminofluorimines from acetylene, N_2F_4, and acetic acid (W. H. Graham; *Abstracts of Papers*, 154th Meeting of the American Chemical Society, Chicago, Illinois, September 1967) was not available at the time this work was carried out. However, the fluorimine C_6H_5–$C(NF_2)(OAc)C(=NF)CH_3$ only fragmented when exposed to sulfuric or fluorosulfonic acid and difluoramine.

(13) T. E. Stevens, *Tetrahedron Letters*, 3017 (1967).

Table II. Reaction of Esters and Difluoramine[a]

Ester[b]	Mmoles	Product	Yield, %[c]
	120		47
	40		29
	42		60
	36		20
	38		9
	33		9
	20		24
	32		53
	45		8

[a] The reaction conditions were 1 ml of 30% fuming sulfuric acid and 1 ml of methylene chloride per gram of ester with excess difluoramine refluxing from a condenser cooled to −80°; reaction temperature was 10–20°; reaction time was 30–90 min. [b] Crude samples of esters were used. [c] Yield of purified product (distillation or silica gel chromatography).

ture was cooled to −130° and 225 cc (STP) of difluoramine was condensed in. The mixture was allowed to warm to room temperature where it was stirred for 6 min, then at 0–5° for 1 hr. The mixture was then distilled through traps at −80 and −110° for 25 min. The desired 1,2,2-tris(difluoramino)propane was obtained from the −80° bath, yield 0.62 g (78%).

Preparation of 1,1,2-Tris(difluoramino)cyclohexane. 1-Acetoxycyclohexene was prepared in the usual way[14] and allowed to interact with N_2F_4 in methylene chloride solution at 200 psi and temperatures up to 80°. The methylene chloride was removed *in vacuo* and the crude adduct was used directly in the following step. To 4 ml of 100% sulfuric acid at −110° was added 1.47 g (6 mmoles) of the 1-acetoxycyclohexene–N_2F_4 adduct in 6 ml of methylene chloride. The solution was degassed at −110°, and HNF_2, 225 cc (STP), was condensed into the flask. The cold bath was removed and the mixture was allowed to warm to ice-bath temperature. After 30 min at ice-bath temperature, the mixture was stirred 1 hr at ambient temperature. The volatile materials were removed *in vacuo* through −25, −80, and −110° traps. The contents of the −25° trap and the reaction flask were poured over ice and extracted into methylene chloride. Evaporation of the methylene chloride left 0.73 g (50%) of product.

1-Phenyl-1,2,2-tris(difluoroamino)propane. 1-Acetoxy-1-phenyl-1-propene, bp 66–67° (0.4 mm), was prepared from 1-phenyl-1-propanone and isopropenyl acetate in the usual way;[14] the sample was a mixture of *cis* and *trans* isomers by nmr spectra and vpc traces. The tetrafluorohydrazine adduct was prepared in methylene chloride solution under 300 psi pressure. The adduct, 1-phenyl-2-acetoxy-1,2-bis(difluoramino)propane, was characterized only by infrared and nmr spectra and was used without purification in the following reaction.

A mixture of 2.5 ml of 100% sulfuric acid, 6 ml of methylene chloride, 1.68 g (6 mmoles) of the above adduct, and 200 cc (STP) of difluoramine was stirred at ice-bath temperature for 1 hr. The excess difluoramine and most of the methylene chloride was removed *in vacuo*, and the residual mixture was poured over crushed ice. The organic products of the hydrolysis were extracted into methylene chloride. The residue obtained upon evaporation of the methylene chloride was chromatographed on a silica gel column packed in pentane–methylene chloride (50:1). Elution of the column with the solvent mixture (15:1) gave 1-phenyl-1,2,2-tris(difluoramino)propane, 0.24 g (15%), as a colorless liquid.

1-Phenyl-1-fluorimino-2,2-bis(difluoramino)propane. A solution of about 0.3 g of 1-phenyl-1,1,1-tris(difluoramino)propane in 10 ml of methylene chloride was stirred at ice-bath temperature, and a solution of 0.52 *N* sodium methoxide in methanol was added dropwise until the reaction mixture was basic; about 2.5 ml of methoxide solution was required. The mixture was then diluted with water and the organic layer was separated. Chromatography of the residue from the methylene chloride extract over a silica gel column packed in pentane–methylene chloride (50:1) gave only 1-phenyl-1-fluorimino-2,2-bis(difluoramino)propane (eluted with 10:1 pentane–methylene chloride) as a colorless liquid. The sample solidified on cooling, but melted at ambient temperature; F^{19} nmr, ϕ −30.7 [$C(NF_2)_2$], −48.2 (C=NF); H^1 nmr, τ 4.63 (phenyl protons), 7.00 (CH_3).

Anal. Calcd. for $C_9H_8N_3F_5$: C, 42.69; H, 3.18; N, 16.60; F, 37.52. Found: C, 42.89; H, 3.00; N, 17.05; F, 37.5

Preparation of Enol Phosphates. The synthesis described below is typical for the preparation of enol phosphates.[15] When the final product could not be distilled the formation of the product was generally followed by infrared analysis. As α-chloro ketone was converted to phosphate the carbonyl absorption band at 5.75 μ decreased in intensity and a new band due to the enol ester appeared at 6.08 μ.

Preparation of 1-Phenyl-1-difluoramino-1-(O,O-diethylphosphoryloxy)-2-fluoriminopropane. 1-Phenyl-1-(O,O-diethylphosphoryloxy)-1-propene was prepared from α-bromopropiophenone and a slight excess of triethyl phosphite (no solvent, 140°, 3 hr); bp 130° (0.1 mm). The addition of tetrafluorohydrazine to this olefin was carried out as usual (in methylene chloride, 50°, 300 psi)[2] and the solution of the adduct was chromatographed on a silica gel column. Elution of the column with methylene chloride–ethyl acetate (50:1) gave the adduct; 10% methanol in methylene chloride eluted the ketophosphonate, O,O-diethyl 2-(1-oxo-1-phenyl)propylphosphonate, which contaminated the sample of the enol phosphate. The adduct was characterized only by nmr spectra. The F^{19} nmr spectrum showed center members of the AB spectrum from the tertiary NF_2 at −964 and −992 cps (40 Mc, internal Freon 11 standard) and a secondary NF_2 multiplet at −1916 to −2052 cps.

A solution of 1.12 g (3 mmoles) of the adduct in 10 ml of methylene chloride was stirred at ice-bath temperature while 5.0 ml of 0.60 *N* sodium methoxide in methanol was added dropwise. The mixture was stirred 30 min at 3°, and was then diluted with water. The methylene chloride layer was separated, washed with water,

(14) H. S. Hagemeyer, Jr., and D. C. Hall, *Ind. Eng. Chem.*, 41, 2920 (1949).

(15) F. W. Lichtenthaler, *Chem. Rev.*, 61, 607 (1961).

and dried ($MgSO_4$). Evaporation of the methylene chloride left 0.92 g of semisolid fluorimino phosphate. The product melted at 62–63° after recrystallization from hexane; F^{19} nmr spectrum, ϕ −34.6 (>C=NF), F_A at −33.6 and F_B at 25.6 (J_{AB} = 572 cps) (CNF_2).

Anal. Calcd for $C_{13}H_{18}N_2F_3O_4P$: C, 44.07; H, 5.12; N, 7.91; F, 16.6. Found: C, 43.45; H, 5.20; N, 7.80; F, 16.35.

1-Phenyl-1,1-bis(difluoramino)-2-fluoriminopropane. A mixture of 5 ml of 100% sulfuric acid and 2.12 g (6 mmoles) of 1-phenyl-1-difluoramino-1-(O,O-diethylphosphoryloxy)-2-fluoriminopropane was degassed at −115°, and 225 cc (STP) of difluoramine was condensed into the 250-ml reaction flask. The −115° bath was removed and was replaced by an ice bath as soon as the sulfuric acid layer began to melt. The mixture was stirred until the pressure drop ceased (about 30 min of stirring). The excess difluoramine was removed from the reaction flask *in vacuo*, and the residual acid solution was quickly poured over crushed ice. The organic products were recovered by methylene chloride extraction. The residue obtained upon evaporation of the methylene chloride was chromatographed on a silica gel column packed with pentane–methylene chloride (20:1). A mixture of pentane and methylene chloride (10:1) eluted 1-phenyl-1,1-bis(difluoramino)-2-fluoriminopropane, 0.65 g, mp 56–57°, from the column.

Anal. Calcd for $C_9H_8N_3F_5$: C, 42.69; H, 3.18; N, 16.60; F, 37.52. Found: C, 43.00; H, 3.41; N, 16.30; F, 38.55.

H^1 nmr spectrum showed aromatic protons at 7.51 ppm and a CH_3 doublet centered at 2.25 ppm; coupling (about 1 cycle splitting) between the methyl and the difluoramino groups was evident; F^{19} nmr spectrum showed a singlet at ϕ −30.7 [$C(NF_2)_2$] and C=NF at −48.3.

Reaction of 1-Acetoxy-1,2-bis(difluoramino)cyclopentane and Sulfuric Acid. A solution of 2.30 g (10 mmoles) of the above acetoxycyclopentane in 10 ml of methylene chloride was added to 4 ml of frozen 100% sulfuric acid. The mixture was degassed and 110 cc (STP) of difluoramine was condensed into the 250-ml reaction flask. The −110° bath was removed and the reaction mixture was stirred at ice-bath temperature for 30 min and at ambient temperature for 30 min. Volatile materials were removed *in vacuo* and the residue was poured over ice. The organic product was extracted with methylene chloride. The residue obtained upon evaporation of the methylene chloride (1.2 g) was purified by silica gel chromatography (elution by methylene chloride–ethyl acetate, 10:1) or by distillation to give 3-difluoramino-2-fluoro-2-azacyclohexanone (**10**). The ^{19}F and ^1H nmr spectra of **10** have been reported;[9] spectral properties of crude and purified material were identical.

Anal. Calcd for $C_6H_7N_2F_3O$: C, 35.72; H, 4.19; N, 16.67; F, 33.9; mol wt, 168. Found: C, 35.78; H, 4.46; N, 17.02; F, 33.6; mol wt (ebullioscopic), 175.

Reaction of 1-Acetoxy-1,2-bis(difluoramino)cyclopentane and Difluoramine. A solution of 18 g (78 mmoles) of the crude adduct of 1-acetoxycyclopentene and tetrafluorohydrazine[2,9] in 20 ml of methylene chloride was added to a mixture of 10 ml of 30% fuming sulfuric acid, 5 ml of methylene chloride, and 400 mmoles of difluoramine (generated from aqueous difluorourea). The difluoramine was allowed to reflux off a −80° condenser. A temperature rise from −4 to +7° occurred during the 20-min addition. The mixture was stirred at 5–12° for 90 min; the excess difluoramine then was vented into a stream of nitrogen. The residue was dumped on crushed ice and diluted with methylene chloride; the methylene chloride solution was washed with water, 10% aqueous sodium bicarbonate, and water. The methylene chloride was evaporated and the residue was chromatographed on silica gel. Elution of the column with pentane–methylene chloride (5:1) gave 1,1,1-tris(difluoramino)cyclopentane (**11**), 3.53 g.

Continued elution of the column gave, in the methylene chloride–ethyl acetate (10:1) eluate, the ketone **10**, 2.18 g.

Reaction of Cyclohexenone and Difluoramine. A solution of 3.84 g (20 mmoles) of cyclohexenone in 40 ml of methylene chloride was added to a mixture of 10 ml of 30% fuming sulfuric acid, 20 ml of methylene chloride, and 200 mmoles of difluoramine at 0°. The difluoramine was allowed to reflux from a cold finger maintained at −80°. After 1 hr at 0–10°, the excess difluoramine was vented, and the residue was poured into ice–water and methylene chloride. The organic layer was washed with water and dilute aqueous sodium bicarbonate solution. The methylene chloride was removed at reduced pressure and the residue was chromatographed on a silica gel column packed in pentane–methylene chloride (98:2). Elution with the sample solvent gave 1,1,3-tris(difluoramino)cyclohexane: 1.73 g; F^{19} nmr, $C(NF_2)_2$ peaks near −800 and −1164 cps (A_2B_2 pattern) (40 Mc, CCl_3F standard) and HC–NF_2 near ϕ −40.6 (doublet) (J_{HF} = ~24 cps).

Anal. Calcd for $C_6H_9N_3F_6$: C, 30.39; H, 3.83; N, 17.72; F, 48.1. Found: C, 30.30; H, 3.84; N, 17.00; F, 49.4.

A New Method for the Directed Conversion of the Phenoxy Grouping into a Variety of Cyclic Polyfunctional Systems

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Abstract: A new synthetic process has been devised and demonstrated for the selective transformation of phenolic substances to a variety of nonbenzenoid, polyfunctional derivatives including 2,5-cyclohexadienones, 3- and 2-cyclohexenones, and cyclohexanones as well as corresponding ketals. The critical part of the method involves the conversion of the phenol to an α-phenoxy-α,α-disubstituted acetic acid derivative and the bromination of the latter as the salt in aqueous solution at 0° to form a bromo lactone in the 1,4-cyclohexadiene series.

Benzenoid rings play an extraordinarily interesting and important role in the synthesis of *nonbenzenoid* as well as benzenoid structures. The most obvious reason for this fact, the ready availability of many benzenoid compounds, is only one of the factors contributing to this importance, however. In general terms the benzenoid unit is a "complex" functional group having a considerable number of synthetically useful characteristics, including the following: (1) a wide variety of functional groups, appendages, and rings can be attached to the ring system by many types of reactions, (2) many reactions are available which allow the interconversion of functional groups, (3) several effective techniques exist for directing chemical attack at specific sites of the benzenoid unit (especially substitution), and (4) the benzenoid system may be "disrupted" or partly saturated to yield cyclic polyfunctional structures.[1]

(1) The term "complex functional group" is used here to mean a standard reactive grouping having several similar sites available for reaction.