be readily explained by the effect of replacing the F^- ions by the larger BF_4^- ions in the ion pairs. In the 2-alkyl carbonium ions the positive charge is located near the end of the chain which permits more efficient solvation by the catalyst and a closer approach by the BF_4^- ions. As the charge enters the middle of the chain, the ion is more efficiently shielded from the BF_4^- ions by its two alkyl groups. This results in slightly greater stability for the 2-alkyl carbonium ions. In addition, evidence has previously been obtained which suggests that the 2-carbonium ion reacts faster with benzene than the internal ones.[6] Since the proton enters the alkylating agent at the center of the chain, which is only two carbon atoms away from the 2 position, this effect combines with the first one to raise the amount of the 2 isomer.

Experimental Section

Materials and Apparatus.—All of the 1-alkenes were obtained from the Aldrich Chemical Co. and the internal olefins were obtained from Farchan Research Laboratories, Cleveland, Ohio. Benzene was dried by azeotropic distillation and anhydrous aluminum chloride was Allied Chemical reagent grade. Anhydrous hydrogen fluoride and gaseous boron trifluoride were obtained from the Matheson Co. and used as received. 2-Phenyldecane was synthesized from acetophenone and *n*-octylmagnesium bromide (Grignard reaction). The tertiary alcohol was dehydrated over potassium bisulfate, and the olefin was hydrogenated to the phenyldecane with palladium on charcoal (5%). The product was about 97% pure as established by glc analysis.

The alkylation reactions were carried out in a 2-l. stainless steel reactor equipped with agitator, thermocouple, cooling coil, pressure gage, and various inlet ports for introducing catalyst and olefin, sampling the reaction mixture, venting the apparatus, and withdrawing the products. All the inlets were provided with stainless steel valves. Strict safety precautions were followed to avoid any contact with liquid or gaseous HF or BF_3.

General Procedure of Alkylation.—Anhydrous benzene (3.9 mol) was charged to the reactor and cooled to 5 to 7° with ice water circulated through the cooling coil. Anhydrous hydrogen fluoride (4 mol), cooled to about −30° with Dry Ice, was then added. All the valves were then closed except the venting valve which was connected through a Tygon tube to a BF_3 lecture bottle which rested on a balance. The calculated amount of BF_3 was then introduced, the valve was closed, and agitation was started. (For alkylations with HF only the BF_3 step was eliminated.) When the temperature reached 0–5°, 0.4 mol of the α olefin in 1 mol of benzene was pumped into the reactor over a 10-min period, using a microbellows pump (Research Appliance Co.). The reaction mixture was aged for 10 min at the same temperature, after which time it was settled for 1 hr to allow separation of the two phases. The catalyst was then drained onto crushed ice, neutralized, and discarded. The alkylate layer was quenched with ice and most of the benzene was removed under suction. The crude alkylbenzene was examined by glc using a Varian Aerograph Model 1800 equipped with an Infotronics electronic integrator. The stainless steel column was 150 ft. × 0.01 in. and was coated with silicon OV7. The crude products were then distilled and the material boiling in the range of the arylalkane was collected. In the presence of HF alone the yields were 87–91% of the theoretical amount. With HF–BF_3 they were 62, 70, and 77% for the C_6, C_8, and C_{10} alkylbenzenes, respectively. After removal of the phenylhexanes, distillation of the residue continued and a fraction boiling at 113–126° (2 mm) was collected (25%). This is close to the boiling point of dodecylbenzene.[8] Its ir spectrum showed it to be primarily dialkylbenzene (12.1 and 12.65 μ). The residues from the alkylations of the higher olefins also showed these bands indicating dialkylation of benzene as a side reaction.

The same procedure was followed for the alkylation of benzene with the internal olefins but the scale of the experiments was only half that of the α olefins.

Registry No.—Benzene, 71-43-2; 1-dodecene, 112-41-4; *trans*-6-dodecene, 7206-13-5; 1-decene, 872-05-9; *trans*-5-decene, 7433-56-9; 1-octene, 111-66-0; *trans*-4-octene, 14850238; 1-hexene, 592-41-6; *trans*-3-hexene, 13269-52-8.

Radical Reactions of Tetrafluorohydrazine. Preparation of Bis(difluoramino)alkanols and Nitrates[1]

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The synthesis of difluoramino-substituted alkanols has been accomplished by the addition of tetrafluorohydrazine to alkenols or to alkenyl esters followed by hydrolysis. The latter method proved satisfactory in giving the alkanols in good yields and purity. It was demonstrated that the alkanols could be nitrated to yield the difluoramino-containing nitrate esters.

Bis(difluoramines) containing reactive functional groups are of considerable interest and importance in the development of NF chemistry. Petry and Freeman[2] have reported the most comprehensive study of the tetrafluorohydrazine (N_2F_4) olefin addition reaction yielding vicinal bis(difluoramines). Olefins examined were composed of two groups: (a) the simple aliphatic olefins and (b) olefins containing various functional groups such as halo, alkoxy, acetoxy, carbonyl, and aryl. The bis(difluoramines) containing acetoxy, alkoxy, and halo substituents were stable, even when attached to carbon atoms bonded to difluoramino groups, while products containing carbonyl, imino, and hydroxyl groups attached in the α position were prone to decompose with loss of hydrogen fluoride or difluoramine.[3,4] The study of bis(difluoramines) containing various functional groups was expanded to include the preparation of a series of bis(difluoramino)alkanols and their corresponding nitrate esters.

Bis(difluoramino)alkanols.—The preparation of bis(difluoramino)alkanols was accomplished by the direct addition of tetrafluorohydrazine (N_2F_4) to alkenols, or by a more preferred method, the addition of N_2F_4 to a suitable ester derivative of the alkenol followed by hydrolysis or methanolysis to give the alcohol adduct.

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(1) This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract DA-01-021 ORD-11909 (Z).

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

(3) S. F. Reed, *ibid.*, **32**, 2893 (1967).

(4) J. P. Freeman, W. H. Graham, and C. O. Parker, *J. Amer. Chem. Soc.*, **90**, 121 (1968).

In most instances the addition reactions were conducted in inert chlorinated solvents at temperatures of 50–100° in both subatmospheric and elevated pressure reactors. Adducts were isolated by distillation and characterized by their infrared spectra and elemental analyses.

The reactions were carried out initially with the alkenols, as depicted below for allyl alcohol. Although the adducts were obtained in satisfactory yields (60–80%), they contained small quantities of impurities which were difficult to remove during purification. The chief impurity in both the crude and distilled products was shown by infrared to be a material containing the carbonyl group. Absorption in the 1750–1690-cm^{-1} range indicated a keto or aldehyde group.

$$CH_2{=}CHCH_2OH + N_2F_4 \longrightarrow F_2NCH_2CH(NF_2)CH_2OH$$

A plausible explanation for the appearance of the carbonyl-containing impurity results from a reaction involving the abstraction of hydrogen from the α position of the alcohol by the difluoramino radical. A variety of radicals are known[5] to abstract hydrogen from alcohols in a similar manner. The nature of the R group, whether alkenyl or bis(difluoramino)alkyl, would be of little importance in this hydrogen abstraction reaction. Subsequent coupling of the α-hydroxylalkyl radical with the difluoramino radical would give the α-(difluoramino)alkanol which, at the reaction temperatures, would probably decompose readily with loss of difluoramine and formation of an aldehyde.[4]

$$RCH_2OH + NF_2 \longrightarrow R\dot{C}HOH + HNF_2$$

$$R\dot{C}HOH + NF_2 \longrightarrow RCH(NF_2)OH$$

$$RCH(NF_2)OH \longrightarrow RCHO + HNF_2$$

Difluoramine was, in fact, observed as a component of the excess gas fraction from these reactions. It accounted for 6–16% of the excess condensable gas fraction, which indicated conversions of N_2F_4 to difluoramine of approximately 1%, although in isolated instances conversions as high as 3% were noted. The vpc analyses showed 1–5% of impurities in the crude alcohol adducts and usually less than 1% in the distilled products. Unfortunately, the distilled samples of the adducts from the allylic alcohols continued to slowly decompose over a period of days with notable discoloration. This behavior of the adducts is attributed to the unstable nature of the carbonyl-containing impurity. Decomposition of the impurity with loss of hydrogen fluoride, followed by further acid-catalyzed decomposition, is thought to account for the observations noted.

$$F_2NCH_2CH(NF_2)CHO \longrightarrow F_2NCH_2C({=}NF)CHO$$

The simple aliphatic alkenols usually were converted to their adducts in good yields, but several other types of unsaturated alcohols did not give the desired adducts. Furfuryl alcohol underwent polymerization prior to the addition of a significant quantity of N_2F_4, and 2-butene-1,4-diol reacted with N_2F_4 mainly by hydrogen abstraction to give a mixture of difluoramines and carbonyl-containing products which were not examined in detail. When divinyl carbinol was treated with N_2F_4, a bis(difluoramine) containing a considerable amount of impurities was obtained in moderate yield (40–55%), along with a high boiling viscous residue which remained after distillation of the bis(difluoramine). The structure of the bis(difluoramine) was never ascertained because of difficulty in removing impurities, and the high-impact sensitive residue was not characterized, although it probably contained some of the desired tetrakis(difluoramine).

To eliminate the difficulties encountered in obtaining bis(difluoramino)alkanols directly from the alkenols, the latter were first converted to suitable ester derivatives, the adduct of the ester was prepared, and the alcohol adducts were generated from the ester adducts *via* hydrolysis or methanolysis reactions. These studies have demonstrated that conversion of the alkenols to their formate or trifluoroacetate derivatives followed by the sequence of reactions shown below is a general method for the synthesis of bis(difluoramino)alkanols. The trifluoroacetates and formates were selected as protective groups because of their ease of preparation and subsequent hydrolysis or methanolysis.

$$CH_2{=}CHCH_2OC({=}O)R + N_2F_4 \longrightarrow F_2NCH_2CH(NF_2)CH_2OC({=}O)R$$

$$R = H \text{ or } CF_3$$

$$F_2NCH_2CH(NF_2)CH_2OC({=}O)R \xrightarrow[\text{methanolysis}]{\text{hydrolysis or}} F_2NCH_2CH(NF_2)CH_2OH + RC({=}O)OH \text{ or } RC({=}O)OCH_3$$

Alkenyl trifluoroacetates were prepared by treating the appropriate alkenols with trifluoroacetic anhydride in the presence of triethylamine or pyridine.[6] A reaction of formic acid with the alcohol in refluxing benzene with azeotropic removal of water gave the formates in yields of 55–70%. Adducts of the esters were prepared by heating the neat esters with N_2F_4 at 80–100° in stainless steel cylinders or in solution under pressure. Characterization data for the ester adducts are presented in Table I. The infrared spectra showed a strong carbonyl absorption near 1785 cm^{-1} (trifluoroacetates) and 1722 cm^{-1} (formates), and NF absorption at 800–1000 cm^{-1}. The presence of by-products arising *via* hydrogen abstraction reactions was not detected in any instance.

In addition to the simple alkenyl esters employed in this study, other esters examined were those prepared from the dienols: divinyl carbinol, 2,4-pentadien-1-ol, and 2,5-hexadien-1-ol. When divinyl carbinol, as its trifluoroacetate, was treated with N_2F_4 under normal reaction conditions, the monoadduct, 3-[1,2-bis(difluoramino)-4-pentenyl] trifluoroacetate, was the major product. Attempts to conduct the reaction under more vigorous conditions led to decomposition of the mixture. The alternate route *via* the formate ester was not possible because of the rearrangement of the ester to 2,4-pentadienyl formate in the preparative reaction. It was later found that, when divinylcarbinyl acetate was treated with N_2F_4, the reaction could be controlled to give either 3-[1,2-bis(difluoramino)-4-pentenyl] acetate or 3-[1,2,4,5-tetrakis(difluoramino)pentyl] acetate as the major products. No suitable techniques were

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[5] R. S. Davidson, *Quart. Rev., Chem. Soc.*, **21**, 249 (1967), and references cited therein.

[6] R. S. Yost and R. D. Shoults, U. S. Patent 3,023,238 (1964).

TABLE I

ALKENYL TRIFLUOROACETATE AND FORMATE ADDUCTS WITH N_2F_4

Adduct of	Registry no.	Yield, %	Bp, °C (mm)	$n^{20}D$
$CF_3C(=O)OCH=CH_2$	24414-89-9	67	41–42 (20)	1.3195
$CF_3C(=O)OCH_2CH=CH_2$	16531-90-1	83	58 (16)	1.3540
$CF_3C(=O)OCH_2C(CH_3)=CH_2$	35209-93-9	59	52 (8)	1.3578
$CF_3C(=O)OCH_2C(CH_2CH_3)=CH_2$	35209-94-0	74	74 (2)	1.3613
$CF_3C(=O)O(CH_2)_4CH=CH_2$	35209-95-1	67	69 (0.3)	1.3762
$CF_3C(=O)OCH_2CH=CHCH_3$	35209-96-2	44	55 (2.5)	1.3612
$CF_3C(=O)OCH(CH=CH_2)_2$[a]	35209-97-3	67	70–71 (2)	
$HC(=O)OCH=CH_2$	30947-80-9	61	40–42 (24)	
$HC(=O)OCH_2CH=CH_2$	21416-97-7	80	36 (1.7)	1.3852
$HC(=O)OCH_2CH=CHCH=CH_2$[b]	35210-00-5[c] 35210-01-6[d]	41	80–82 (0.8)	
$HC(=O)OCH_2CH=CHCH_2CH=CH_2$[b]	35210-02-7[e] 35210-03-8[f]	70	88–89 (0.6)	

[a] Bis(difluoramine). [b] Mixture of bis(difluoramines). [c] 3-Pentenyl adduct. [d] 2-Pentenyl adduct. [e] 2-Hexenyl adduct. [f] Tetrakis adduct.

found for the hydrolysis of either acetate ester adduct to the alcohol.

The reaction of N_2F_4 with 2,4-pentadienyl formate gave only a mixture of bis(difluoramino)alkenyl formates arising from the addition of 1 mol of N_2F_4 to the conjugated double bond system of the ester through either 1,2 or 1,4 addition. Further addition of a second mole of N_2F_4 was not realized under the experimental conditions.[7] In contrast, when 2,5-hexadienyl formate was treated with N_2F_4, both the 5,6-bis(difluoramino)-2-hexenyl formate and the 2,3,5,6-tetrakis(difluoramino)hexyl formate could be obtained as major products by controlling the experimental conditions. These two reactions demonstrate the difference in relative ease of N_2F_4 addition to nonconjugated dienes over the conjugated dienes. The difficulty in obtaining completely saturated products from the conjugated dienes has been attributed to the reversible nature of the reaction.[2]

$$CH_2{=}CHCH{=}CHCH_2OOCH + N_2F_4 \longrightarrow F_2NCH_2CH{=}CHCH(NF_2)CH_2OOCH + F_2NCH_2CH(NF_2)CH{=}CHCH_2OOCH$$

It is important also to point out that isolation and purification of the mixed adducts obtained from the N_2F_4–diene reactions were extremely difficult because of their similarity of properties (bis adducts) and the unusual high boiling points and ultrasensitivity of the tetrakis adducts. While totally pure individual adducts were not realized in these instances, all the analytical evidence available, including vpc data, is indicative of the presence of the designated products.

Treatment of the ester adducts with anhydrous methanol at 50 to 70° with or without an acid catalyst such as p-toluenesulfonic acid or Amberlyst 15[8] gave the alcohol adducts in 70–90% yield after distillation. Catalysts were beneficial in increasing the rate of methanolysis of the esters. The alcohols (Table II) were shown to be of high purity by vpc analyses and displayed no tendency to decompose on storage. Characteristic absorption bands at 3400–3500 cm^{-1} and 800–1000 cm^{-1} were noted in their infrared spectra.

TABLE II

DIFLUORAMINOALKANOLS

Alkanol	Registry no.	Yield, %	Bp, °C (mm)	$n^{20}D$
1,2-Bis(difluoramino)-ethanol	13084-47-4	87	40–42 (18)	1.3948
2,3-Bis(difluoramino)-propanol	16531-91-2	89	44 (3)	1.3967
2-Methyl-2,3-bis(difluoramino)propanol	21678-71-7	73	43 (1)	1.3952
2,3-Bis(difluoramino)-butanol	24403-11-0	78	58 (1)	1.3990
1,2-Bis(difluoramino)-pentan-3-ol	24403-12-1	90	85–87 (1)	
5,6-Bis(difluoramino)-hexan-1-ol[a]	24403-13-2	79		
1,2,4,5-Tetrakis(difluoramino)pentan-3-ol[a]	21828-55-7	65		
4,5-Bis(difluoramino)-2-penten-1-ol[a,b]	35210-11-8			
2,4-Bis(difluoramino)-3-penten-1-ol	35210-12-9	77		
2,3,5,6-Tetrakis(difluoramino)hexan-1-ol[a]	35210-13-0	69		
2-Difluoramino-2-difluoraminomethyl-propane-1,3-diol[a]	35210-14-1	71		

[a] Decomposed on attempted distillation. [b] A mixture of bis adducts.

An alternate method of effecting the generation of the alcohol adducts was to hydrolyze the esters in a mixture of methanol and dilute (5%) mineral acid (HCl or H_2SO_4). In most instances the hydrolysis reactions were satisfactory, giving slightly lower yields than the methanolysis reactions; however, some decomposition of the adducts occurred in isolated instances, as evidenced by low fluorine and high nitrogen analyses of the alcohols. It was further shown that the use of concentrated hydrochloric acid–methanol mixtures resulted in hydrolysis and partial conversion of the alcohols to the corresponding chlorides, as evidenced by the unusually high chlorine content (7–9%) of the hydrolysis products. This side reaction was not apparent when dilute acid was used. These factors, along with the usually lower yields of the alcohol adducts (50–85%) obtained from the acid hydrolysis,

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(7) In reactions conducted at temperatures of 150–200° and pressures exceeding 300 psi, the tetrakis(difluoramino)pentyl formate was obtained in excellent yield. Studies conducted by Dr. K. E. Johnson of Rohm and Haas Co., Redstone Research Laboratories, Huntsville, Ala.

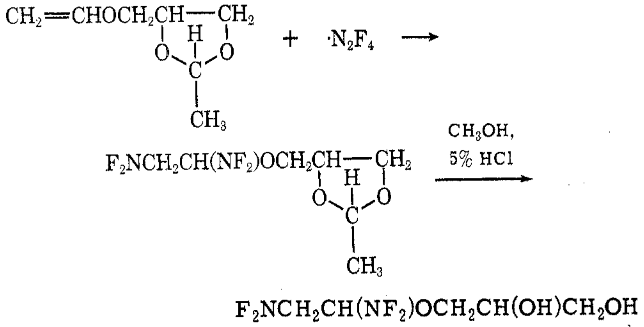
(8) Ion exchange resin, trademark of the Rohm and Haas Co., Philadelphia, Pa.

TABLE III
BIS(DIFLUORAMINO)ALKYL NITRATES

Nitrate	Registry no.	Yield, %	Bp, °C (mm)	$n^{20}D$
$F_2NCH_2CH(NF_2)CH_2ONO_2$	18804-80-3	85.5	45–46 (2)	1.3996
$F_2NCH_2C(CH_3)(NF_2)CH_2ONO_2$	35210-16-3	97	40–41 (1)	1.4055
$F_2NCH_2C(CH_2ONO_2)(NF_2)CH_2ONO_2$	35210-17-4	96.5		1.4380
$F_2NCH_2CH(NF_2)OCH_2CH(ONO_2)CH_2ONO_2$	35210-18-5	98.7		1.4303

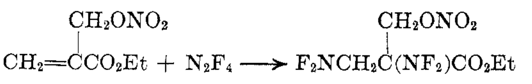
made the methanolysis technique the preferred method for generating the alcohol adducts.

Another example of employing protective groups in the alkenol–N_2F_4 reactions was demonstrated with the use of acetals. Treatment of 2-methyl-4-vinyloxymethyl-1,3-dioxolane with N_2F_4 gave 2-methyl-4-[1,2-bis(difluoramino)ethoxymethyl]-1,3-dioxolane in excellent yields (85–90%). Hydrolysis of this adduct in methanol–5% HCl gave 3-[1,2-bis(difluoroamino)-ethoxy]-1,2-propanediol (86%).



Similarly, when methyl divinylcarbinylformal was treated with N_2F_4, the products isolated were methyl 3-[1,2-bis(difluoramino)-4-pentenyl]formal and methyl 3-[1,2,4,5-tetrakis(difluoramino)pentyl]formal. Both adducts were readily hydrolyzed to the corresponding alcohols with a mixture of methanol–5% HCl at room temperature.

Bis(difluoramino)alkyl Nitrates.—Reactions of nitrate esters of alkenols with N_2F_4 were not considered a promising route to the mixed NF nitrates because of several factors. The thermal instability imposed by the nitrate group precludes any attempt to form the adduct in many instances. In others, unless reactions go essentially to completion and by-product formation is minimal, the purification of the product is difficult and often hazardous, since these type compounds possess high thermal and impact sensitivities. Only in isolated instances was even partial success realized in forming the adduct of unsaturated nitrates. When ethyl (α-nitratomethyl)acrylate was treated with N_2F_4 under relatively mild conditions, a crude product was obtained whose composition approximated that of the expected adduct. Attempts to distil the crude mixture resulted in decomposition. A similar reaction of



$$CH_2{=}\overset{\displaystyle CH_2ONO_2}{\overset{|}{C}}CO_2Et + N_2F_4 \longrightarrow F_2NCH_2\overset{\displaystyle CH_2ONO_2}{\overset{|}{C}}(NF_2)CO_2Et$$

petrin methacrylate (methacrylate of pentaerythritol trinitrate) and N_2F_4 gave the adduct which analyzed satisfactorily. Presumably the ease of addition of N_2F_4 to the acrylate ester permitted mild conditions to be employed and eliminated many of the potential side reactions which occur in operating at the higher temperatures necessary for many olefin–N_2F_4 reactions.

The method of choice for preparing mixed NF_2–ONO_2 substituted compounds was to first prepare the NF_2-containing alcohols and then nitrate by suitable means. It has been demonstrated that this preparative procedure is successful in giving the desired mixed products in excellent yields and purity. The nitrate esters of bis(difluoramino)alkanols were prepared conveniently by a mixed acid nitration procedure. Nitration was carried out in methylene chloride at temperatures of 15–45° employing an excess of a 2:1 HNO_3–H_2SO_4 mixture.

The diols were treated in the same manner as the simple alcohols, except that the reaction time was extended by approximately one-half hour in the case of the diols. Although the products were isolated in a crude state, they were usually pure, as shown by satisfactory elemental analyses and infrared spectra. Their spectra were characterized by strong NF absorption at 800 to 1000 cm^{-1} and ONO_2 absorption near 1160 and 1265 cm^{-1}. 1,2-Bis(difluoramino)ethyl nitrate, which decomposed prior to analysis, was the only unstable product. This is not surprising in view of the observations discussed earlier in this paper. Accordingly, the nitrate group may be classed with carbonyl, imino, and hydroxyl groups as α substituents in difluoramines which lead to unstable products (Table III).

$$F_2NCH_2CH(NF_2)CH_2OH + HNO_3\text{–}H_2SO_4 \xrightarrow{CH_2Cl_2} F_2NCH_2CH(NF_2)CH_2ONO_2$$

This study has demonstrated that bis(difluoramino)-alkanols can be prepared in high yields and of good purity employing easily hydrolyzable esters. While alkenols can be reacted directly with N_2F_4 to give the adducts, it was shown that in these reactions hydrogen abstraction takes place to a limited extent, yielding small quantities of by-products not easily removed from the desired alkanols. Formation of mixed NF_2–ONO_2 substituted compounds was accomplished by a general nitration procedure. α-Nitrato-substituted difluoramines were found to be unstable.

Experimental Section[9]

The alkenols employed in this work were purchased from commercial sources and used as received except for divinyl carbinol, which was prepared by the method of Ramsden.[10] Tetrafluorohydrazine of greater than 95% purity and containing volatile CF compounds as impurities was used for all addition reactions. Infrared spectra were obtained on a Perkin-Elmer Infracord spectrophotometer using a sodium chloride prism. ^{19}F nmr spectra were obtained with a Varian Associates Model V-3000-B high-resolution spectrometer with a 40 Mc probe, with trifluoroacetic acid as an internal standard. All gas chromatographic work was carried out on an Aerograph Instrument

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(9) All boiling points are uncorrected.

(10) H. E. Ramsden, J. R. Leebrick, S. D. Rosenberg, E. H. Miller, J. J. Walburn, A. E. Balent, and R. Cserr, *J. Org. Chem.*, **22**, 1602 (1957).

Model A-100-C using a 5′-dinonyl phthalate on Chromosorb column at 50 to 100°, unless otherwise noted.

The nature of the reaction of tetrafluorohydrazine with organic substrates implies that caution be exercised in the experimental work. It is essential that oxygen be rigorously excluded from all reaction mixtures to prevent explosions. The experimental work was conducted in remote areas, using remote-controlled equipment insofar as possible as a safety precaution to minimize personnel exposure. In addition, care in handling of products reported, particularly the mixed NF_2–ONO_2 substituted compounds, is necessary since they are impact sensitive in most instances.

In many reactions final purification of several products was not attempted. Since most of these materials analyzed satisfactorily as obtained from the reactions so that characterization was not in doubt, their final purification was not considered necessary. The main concern with these highly thermal and impact-sensitive materials was the hazardous nature of the purification operation, which required the distillation of a high boiling liquid.

Allyl Alcohol–N_2F_4.—To a 100-ml round-bottomed flask fitted with a magnetic stirrer was introduced 11.6 g (0.2 mol) of allyl alcohol and 25 ml of carbon tetrachloride. The flask was connected to a glass manifold system containing a 2-l. expansion bulb, and the total system was deaerated by passing through three freeze–thaw cycles while under vacuum. Tetrafluorohydrazine (15.0 g, 144 mmol) was charged into the system and the mixture was heated to 90° for a period of 4.3 hr. Analysis of the residual condensable gas fraction by mass spectroscopy showed that 8.68 g (83 mmol) of N_2F_4 has reacted. Also present in the condensable gas fraction was difluoramine (0.18 g, 3 mmol). After removal of the condensable gases and the introduction of air, the flask containing the mixture was placed on a rotatory evaporator to remove the solvent and unreacted alcohol. The crude residue was analyzed by its infrared spectrum: 3450 (s), 1718 (w), and 800–1000 (s) cm^{-1}. Gas chromatography showed the presence of one significant impurity (2%), along with several minor ones. Distillation of the crude material gave a water-clear distillate [bp 47–48° (4 mm), n^{20}_{D} 1.3993] in the amount of 20.2 g (81%). Infrared analysis showed a pronounced decrease in the carbonyl absorption. A second vpc analysis showed a significant decrease in the impurities. On standing overnight a slight discoloration was noted in the sample. This discoloration increased over a period of several days, along with some etching of the glass container. Redistillation of the sample effected an improvement in the stability of the product; however, over a period of several days, the discoloration was again noted.

Anal. Calcd for $C_3H_6F_4N_2O$: C, 22.22; H, 3.70; F, 46.91; N, 17.58. Found: C, 22.49; H, 3.95, F, 46.72; N, 17.51.

Allyl Trifluoroacetate–N_2F_4.—The preparation of 2,3-bis(difluoramino)propyl trifluoroacetate is typical of the N_2F_4 addition reactions of the neat alkenyl esters. To a 1-l. stainless steel evacuated reactor fitted with pressure gage, valve, and a ball joint for attachment to a vacuum line was charged 7.7 g (0.05 mol) of allyl trifluoroacetate (previously degassed) and 10.4 g (0.1 mol) of N_2F_4 while being cooled externally in a liquid nitrogen bath. After disconnection from the vacuum line, the reactor was allowed to warm to ambient temperature and then placed in an oil bath and heated to 100° for a period of 5 hr, during which time the pressure dropped from a maximum of 56 to 26 psi. On cooling, the gaseous contents of the reactor were removed under vacuum into a series of cold traps located on a vacuum manifold. The product fraction was collected in a Dry Ice–acetone cooled trap. The liquid fraction obtained from this trap was distilled to give 10.09 g (77.2%) of 2,3-bis(difluoroamino)propyl trifluoroacetate, bp 58° (16 mm), n^{20}_{D} 1.3540.

Anal. Calcd for $C_5H_5F_7N_2O_2$: C, 23.21; H, 1.94; F (hydrolyzable), 51.60; N, 10.85. Found: C, 23.05; H, 1.99; F (hydrolyzable), 51.47; N, 10.69.

Allyl Formate–N_2F_4.—Allyl formate (8.6 g, 100 mmol) previously degassed was condensed into a stainless steel reactor with N_2F_4 (14.66 g, 141 mmol) and heated to 90° for a period of 6 hr. Isolation in the usual manner gave 16.27 g of liquid residue which was distilled at reduced pressure to give 15.38 g (80%) of the adduct: bp 36° (1.7 mm); n^{20}_{D} 1.3852, d^{23}_{4} 1.442; ir 1723 and 800–1000 cm^{-1}.

Anal. Calcd for $C_4H_6F_4N_2O_2$: C, 26.66; H, 3.34; F, 42.22; N, 15.56. Found: C, 26.51; H, 3.41; F, 42.37; N, 15.49.

2,4-Pentadienyl Formate–N_2F_4.—Under similar experimental conditions 5.6 g (56 mmol) of 2,4-pentadienyl formate was treated with 10.4 g (100 mmol) of N_2F_4 at 100° for a period of 5 hr. After cooling and degassing the reactor, it was opened and the liquid contents were removed mechanically. Distillation at reduced pressure gave 4.69 g of a clear product, bp 80–82° (0.8 mm), shown by vpc analysis to be a mixture of two components in near equal portions. The ^{19}F nmr spectrum showed two triplets of near equal area centered at −5397 and −5257 Hz representing the $-CH_2NF_2$ groups and absorption at −4740 Hz indicative of a $-CHNF_2$ group; ir spectra showed 1722 and 800–1000 cm^{-1}. From these data the products were determined to be 4,5-bis(difluoramino)-2-pentenyl formate and 2,5-bis(difluoramino)-3-pentenyl formate arising from 1,2 and 1,4 addition of N_2F_4 to the conjugated double bond of 2,4-pentadienyl formate. There was no evidence to support the formation or presence of the tetrakis(difluoramine) in this reaction.

Anal. Calcd for $C_6H_8F_4N_2O_2$: C, 33.30; H, 3.70; F, 35.14; N, 12.97. Found: C, 33.08; H, 4.05; F, 35.43; N, 13.41.

2-Methyl-4-vinyloxymethyl-1,3-dioxolane-N_2F_4.—To a deaerated solution of 8.6 g (60 mmol) of 2-methyl-4-vinyloxymethyl-1,3-dioxolane in 25 ml of CCl_4 contained in a thick-walled glass reactor attached to a high pressure manifold system was added 10.4 g (100 mmol) of N_2F_4. The mixture was heated to 70° for 5 hr with a maximum pressure of 68 psi being obtained. On cooling, the excess N_2F_4 was removed, air was introduced into the reactor, and finally the contents were removed. The CCl_4 was removed on a rotatory evaporator and the residue was distilled through a short path column to give 14.0 g (94%) of 2-methyl-4-[1,2-bis(difluoramino)ethoxymethyl]-1,3-dioxolane [bp 55–56° (0.02 mm)] as a heavy oil.

Anal. Calcd for $C_7H_{12}F_4N_2O_3$: C, 33.87; H, 4.83; F, 30.65; N, 11.29. Found: C, 33.57; H, 4.74; F, 30.44; N, 11.49.

Methyldivinylcarbinylformal–N_2F_4.—Methyldivinylcarbinylformal (2.0 g, 15.6 mmol) in 25 ml of CCl_4 contained in a thick-walled glass reactor was treated with 5.2 g (50 mmol) of N_2F_4 at 90° for 5 hr at a maximum pressure of 101 psi. Following the usual isolation procedure, 4.2 g of a mixture of products was obtained as determined by vpc analysis. Distillation at reduced pressure gave 1.31 g of a product: bp 51° (2.2 mm); n^{20}_{D} 1.4026; vpc 98%; ir 1640 (w) and 800–1000 (s) cm^{-1}. These data, in conjunction with the elemental analysis, confirmed the identity of the product to be methyl-3-[1,2-bis(difluoramino)-4-pentenyl]formal.

Anal. Calcd for $C_7H_{12}F_4N_2O_2$: C, 36.21; H, 5.17; F, 32.75; N, 12.06. Found: C, 36.15; H, 5.30; F, 32.55; N, 12.03.

The residue [2.72 g; n^{20}_{D} 1.3967; vpc 95%; ir 800–1000 (vs) cm^{-1}] was considered to represent the compound methyl-3-[1,2,4,5-tetrakis(difluoramino)pentyl]formal, although the elemental analysis was slightly high in carbon.

Methanolysis of Bis(difluoramino)alkyl Trifluoroacetates.—A typical transesterification is described for the preparation of 2,3-bis(difluoramino)propanol. To a 100-ml round-bottomed flask fitted with magnetic stirrer and distillation assembly was introduced 5.95 g (0.21 mol) of 2,3-bis(difluoramino)propyl trifluoroacetate and 25 ml of anhydrous methanol. The flask was heated intermittently by means of 65–67° hot water bath during a period of 3 hr. A total of 26.0 g of methyl trifluoroacetate (96%) distilled from the reaction mixture. The remaining residue was distilled to give 30.5 (89%) of 2,3-bis(difluoramino)propanol: bp 44° (3 mm); ir 3425 (s) and 800–1000 (vs) cm^{-1}.

Anal. Calcd for $C_3H_6F_4N_2O$: C, 22.22; H, 3.70; F, 46.91; N, 17.28. Found: C, 22.06; H, 3.84; F, 46.66; N, 17.58.

In a series of methanolysis reactions 2,3-bis(difluoramino)propanol was obtained in yields of 70–89%. Experimental data on the typical methanolysis of other alkenyl trifluoroacetate adducts are presented in Table IV.

TABLE IV
METHANOLYSES OF BIS(DIFLUORAMINO)ALKYL TRIFLUOROACETATES

Alkyl group	Time, hr	Temp, °C	% methyl ester	% alcohol adduct
$F_2NCH_2CH(NF_2)-$	3	50	82	87
$F_2NCH_2C(NF_2)(CH_3)CH_2-$	2.5	50	84	73
$F_2NCH_2CH(NF_2)CH(CH_2CH_3)-$	3.5	55	89	90
$F_2NCH_2CH(NF_2)(CH_2)_4-$	3	55	81	79
$CH_3CH(NF_2)CH(NF_2)CH_2-$	3	50	85	78
$F_2NCH_2CH(NF_2)CH(CH{=}CH_2)-$	4	50	72	76

TABLE V

HYDROLYSIS OF 2,3,5,6-TETRAKIS(DIFLUORAMINO)HEXYL FORMATE

Formate	MeOH, ml	H_2O, ml	Catalyst	Time, hr	Temp, °C	Yield, %
6.68 g (50 mmol)	35	30	5 ml of HCl	3.0	27	73
	40	30	Amberlyst 15, 1 g	3.0	27	76
	40	30	*p*-TSA, 1 g	3.0	27	71.5
	40		10 ml of concd HCl	0.5	27	20
	40		10 ml of concd HCl	1.0	27	16

Hydrolysis of 2,3-Bis(difluoramino)propyl Formate.—A typical hydrolysis reaction is described. To a mixture of 100 ml of methanol, 95 ml of H_2O and 5 ml of concentrated HCl was added slowly 19.0 g (100 mmol) of 2,3-bis(difluoramino)propyl formate. There was no noticeable exotherm. After stirring at ambient temperature for 24 hr, the excess methanol was removed on a rotatory evaporator and the aqueous solution was extracted with ether. The combined ether extracts were washed with water and dried over anhydrous $MgSO_4$, and the ether was removed by evaporation. Distillation of the liquid residue gave 2,3-bis(difluoramino)propanol: 13.65 g, 84%; bp 45° (3 mm); $n^{20}\text{D}$ 1.3964.

Anal. Calcd for $C_3H_6F_4N_2O$: C, 22.22; H, 3.70; F, 46.91; N, 17.28. Found: C, 22.15; H, 3.60; F, 46.61; N, 17.43.

Hydrolysis of 2,3,5,6-Tetrakis(difluoramino)hexyl Formate.—The hydrolysis of 2,3,5,6-tetrakis(difluoramino)hexyl formate was carried out by several methods, as shown in Table V. Catalysts employed were dilute and concentrated HCl, Amberlyst 15, and *p*-toluenesulfonic acid. Only when concentrated HCl was used did the yield of the alcohol decrease. In these instances the formate ester was converted in part to the chloride, as shown by the high chlorine content (>8%) of the product mixtures. Gas chromatography showed the chloride to account for 80–85% of the product fraction, with the alcohol being present in yields of 15–20%.

Hydrolysis of 2-Methyl-4-[1,2-bis(difluoramino)ethoxymethyl]-1,3-dioxolane.—A mixture of 13.8 g (5 mmol) of 2-methyl-4-[1,2-bis(difluoramino)ethoxymethyl]-1,3-dioxolane, 100 ml of methanol, 95 ml of water, and 5 ml of concentrated HCl was stirred at room temperature for a period of 24 hr. Removal of the methanol on a rotatory evaporator followed by ether extraction of the aqueous solution gave 9.65 g (87%) of a viscous oily liquid, with an ir of 3450–3500 (s) and 800–1000 (s) cm^{-1}. The infrared spectral data and the elemental analyses confirmed the structure to be the desired diol 3-[1,2-bis(difluoramino)-ethoxy]-1,2-propanediol.

Anal. Calcd for $C_5H_{10}F_4N_2O_3$: C, 27.03; H, 4.50; F, 34.24; N, 12.63. Found: C, 27.33; H, 4.67; F, 34.03; N, 12.77.

Ethyl (α-Nitratomethyl)acrylate–N_2F_4.—A solution of 2.19 g (12.5 mmol) of ethyl (α-nitratomethyl) acrylate in 25 ml of CCl_3 contained in a thick-walled, high-pressure glass reactor was attached to a high-pressure manifold and deaerated, and 10.4 g (100 mmol) of N_2F_4 was introduced into the system. The mixture was heated to 80° for a period of 3.5 hr at a maximum pressure of 85 psi. On cooling, the excess N_2F_4 was removed, the system was opened to the atmosphere, and the reactor was removed from the manifold. Isolation in the usual manner gave 1.5 g of a viscous oily liquid showing high impact sensitivity (ir 1747, 1606, 1274, and 800–1000 cm^{-1}).

Anal. Calcd for $C_6H_9F_4N_3O_5$: C, 25.80; H, 3.23; F, 27.23; N, 15.06. Found: C, 26.80; H, 3.79; F, 26.94; N, 15.01.

Petrin Methacrylate–N_2F_4.—Petrin methacrylate (2.0 g, 6 mmol) in 25 ml of CCl_4 contained in a 100-ml flask was placed on a high-pressure manifold system, deaerated, and treated with 10.4 g (100 mmol) of N_2F_4 at ambient temperature over a period of 2 hr (maximum pressure was 78 psi). After the usual isolation procedure, 2.8 g of a clear viscous oil was obtained (ir 1754, 1608, 1271, and 800–1000 cm^{-1}).

Anal. Calcd for $C_9H_{13}F_4N_5O_{11}$: C, 24.37; H, 2.93; F, 17.12; N, 15.8. Found: C, 24.01; H, 3.06; F, 17.50; N, 16.1.

Nitration of 2,3-Bis(difluoramino)propanol.—To a 50-ml three-necked flask (appropriately shielded) fitted with a condenser (Drierite drying tube), dropping funnel, magnetic stirrer, and air sparging tube was added 14.0 g (0.2 mmol) of 90% fuming nitric acid. The acid was air sparged until it became clear (approximately 15 min), after which the tube was replaced by a thermometer, an ice water bath was placed around the flask, and (with stirring) 10.0 g (0.1 mol) of 96% sulfuric acid was added *via* the dropping funnel. Then 10 ml of methylene chloride was added, followed by the slow addition of a solution of 16.2 g (0.1 mol) of 2,3-bis(difluoramino)propanol in 25 ml of methylene chloride. The temperature of the mixture was raised to 40–43° and the mixture was refluxed for a period of 15–20 min. On cooling the mixture was transferred to a separatory funnel containing additional methylene chloride. The acid layer was separated and the methylene chloride solution was washed with cold water, cold saturated sodium bicarbonate, and again with cold water, and then was dried over anhydrous $MgSO_4$. After filtration the solvent was removed on a rotatory evaporator to give an oily residue: 18.92 g, 85.6%; bp 45–46° (2 mm); $n^{20}\text{D}$ 1.3996; $d^{23}{}_4$ 1.533; ir 1610, 1270, and 800–1000 cm^{-1}.

Anal. Calcd for $C_3H_5F_4N_3O_3$: C, 17.40; H, 2.43; F, 36.70; N, 20.29. Found: C, 17.66; H, 2.66; F, 36.86; N, 20.20.

Nitration of 3-[1,2-Bis(difluoramino)ethoxy]-1,2-propanediol.—Under similar experimental conditions, 5.6 g (15 mmol) of 3-[1,2-bis(difluoramino)ethoxy]-1,2-propanediol was added to a mixture of 8.8 g (125 mmol) of 90% nitric acid and 12.3 g (67 mmol) of 96% sulfuric acid. The mixture was refluxed for a period of 45 min. A 7.7-g (98%) portion of a viscous oily residue was obtained after washing, drying, and removal of solvent. The product was identified as the dinitrate of 3-[1,2-bis(difluoramino)ethoxy]1,2-propanediol: $n^{20}\text{D}$ 1.4303; $d^{23}{}_4$ 1.530; ir 1605, 1275, and 800–1000 cm^{-1}.

Anal. Calcd for $C_5H_8F_4N_4O_7$: C, 19.24; H, 2.58; F, 24.35; N, 17.95. Found: C, 19.05; H, 2.66; F, 24.53; N, 17.70.

Registry No.—2-Methyl-4-[1,2-bis(difluoroamino)-ethoxymethyl]-1,3-dioxolane, 35210-19-6; methyl-3-[1,2-bis(difluoroamino)-4-pentenyl]formal, 35210-20-9; methyl-3-[1,2,4,5-tetrakis(difluoroamino)pentyl]formal, 35210-21-0; 3-[1,2-bis(difluoroamino)ethoxy]-1,2-propanediol, 17686-77-0; ethyl (α-nitratomethyl)acrylate–N_2F_4 adduct, 35210-23-2; petrin methacrylate–N_2F_4 adduct, 35210-24-3; tetrafluorohydrazine, 10578-16-2.

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