Radical Reactions of Tetrafluorohydrazine. Allylic Halides[1]

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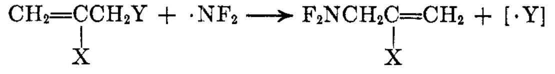
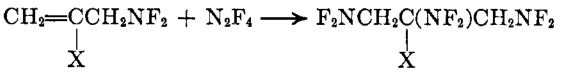
Attack of a difluoramino radical on certain allylic bromides and iodides has been shown to effect the elimination of the halogen with formation of an allylic difluoramine. Further reaction of the allylic difluoramine with tetrafluorohydrazine leads to the formation of 1,2,3-tris(difluoramines). The reaction appears to be general in scope for most of these allylic halides.

Tetrafluorohydrazine (N_2F_4) is known to undergo a number of reactions with organic substrates[2] *via* a radical mechanism including its addition to olefins.[3] Studies[4] conducted in this laboratory have demonstrated that the tetrafluorohydrazine–olefin addition reaction is of a general nature yielding bis(difluoramines). Continued interest led to a study of the reaction with allylic halides as the olefin substrates. Although allyl chloride was known[4] to react with N_2F_4 to yield the normal addition product, 2,3-bis(difluoramino)propyl chloride, the use of allylic bromides and iodides revealed that the reaction took an alternate course to yield allylic difluoramines[5] and more highly substituted products with their ratio depending upon the substrate and reaction conditions employed. The transformation may be described as shown where X is represented by H, CH_3, C_6H_5, Br, CN, and $CO_2CH_2CH_3$ and Y may be Br or I.



$$\mathrm{CH_2{=}\underset{\displaystyle X}{\underset{|}{C}}CH_2Y + \cdot NF_2 \longrightarrow F_2NCH_2\underset{\displaystyle X}{\underset{|}{C}}{=}CH_2 + [\cdot Y]}$$



$$\mathrm{CH_2{=}\underset{\displaystyle X}{\underset{|}{C}}CH_2NF_2 + N_2F_4 \longrightarrow F_2NCH_2\underset{\displaystyle X}{\underset{|}{C}}(NF_2)CH_2NF_2}$$

In the case of those reactions involving allylic bromides further complications are observed due to the addition of the liberated bromine to sites of unsaturation resulting in the formation of mixed bromodifluoramino-substituted products as well as tribromopropanes; hence, lower yields of the allyl difluoramines are obtained in these instances. In contrast employment of allylic iodides reduce the complexity through elimination of the halogen addition products, since the liberated iodine does not enter the reaction by adding to sites of residual unsaturation. For this reason the iodides are preferred and were examined to the greater extent. To some degree the reactions could be controlled to yield predominantly either the mono- or tris(difluoramines). It was also possible to isolate the allylic difluoramine and by subsequent reaction with N_2F_4 to convert it into the 1,2,3-tris(difluoramine).

These reactions may be conducted under a variety of experimental conditions including flow, static (neat), or solution systems at either subatmospheric or elevated pressures. For the preparation of allylic difluoramines, the flow and solution systems (the latter at subatmospheric pressure) are preferred since under other conditions the yields of more highly substituted products are increased. Reaction temperatures depend upon other conditions being approximately 200° for flow reactions, and 50–100° for all others. Inert solvents such as chloroform, carbon tetrachloride, and chlorobenzene were found most suitable for the solution reactions.

The products were isolated by distillation and identified by their infrared spectra and elemental analysis. In certain instances the fluorine and proton nmr spectra were obtained. Characterization data for the various allylic difluoramines are reported in Table I while similar data for the tris(difluoramines) are shown in Table II.

A proposed mechanism consistent with the formation of the observed products is shown in Scheme I as illustrated by the use of allyl bromide. Difluoramino radicals formed on disassociation of tetrafluorohydrazine attack allyl bromide with the formation of the radical intermediate **1**, which has three modes of reaction. Through coupling with a second difluoramino radical the mixed product **2** would arise, by displacement of a bromine atom allyldifluoramine (**3**) is formed, and by coupling with a bromine radical the mixed product **4** is obtained. The major reaction is considered to be the displacement of a bromine atom and formation of allyldifluoramine (**3**) which may undergo further reactions. Compound **4** is thought to arise primarily by addition of bromine to the allyldifluoramine. Whether the mixed product represents both **2**

SCHEME I

$$\mathrm{N_2F_4 \rightleftharpoons 2\cdot NF_2} \tag{1}$$

$$\mathrm{CH_2{=}CHCH_2Br + \cdot NF_2 \rightleftharpoons \underset{1}{F_2NCH_2\dot{C}HCH_2Br}} \tag{2}$$

$$\mathrm{\underset{1}{F_2NCH_2\dot{C}HCH_2Br} + \cdot NF_2 \longrightarrow \underset{2}{F_2NCH_2CH(NF_2)CH_2Br}} \tag{3}$$

$$\mathrm{\underset{1}{F_2NCH_2\dot{C}HCH_2Br} \longrightarrow \underset{3}{F_2NCH_2CH{=}CH_2} + \cdot Br} \tag{4}$$

$$\mathrm{\underset{1}{F_2NCH_2\dot{C}HCH_2Br} + \cdot Br \longrightarrow \underset{4}{F_2NCH_2CH(Br)CH_2Br}} \tag{5}$$

$$\mathrm{\underset{3}{F_2NCH_2CH{=}CH_2} + Br_2 \longrightarrow \underset{4}{F_2NCH_2CH(Br)CH_2Br}} \tag{6}$$

$$\mathrm{\underset{3}{F_2NCH_2CH{=}CH_2} + N_2F_4 \longrightarrow \underset{5}{F_2NCH_2CH(NF_2)CH_2NF_2}} \tag{7}$$

$$\mathrm{CH_2{=}CHCH_2Br + Br_2 \longrightarrow \underset{6}{BrCH_2CH(Br)CH_2Br}} \tag{8}$$

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[1] This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Alabama under Contract 02-021 ORD-11878.

[2] J. P. Freeman, "Free Radicals in Inorganic Chemistry," Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p 123.

[3] A. J. Dijkstra, Ph.D. Thesis, University of Leiden, 1965. H. Cerfontain, *J. Chem. Soc.*, 6602 (1965); A. L. Logothetis, U. S. Patents 3,196,167 (Aug 20, 1965) and 3,215,709 (Nov 2, 1965); A. L. Logothetis and G. N. Sausen, *J. Org. Chem.*, **31**, 3689 (1966).

[4] R. C. Petry and J. P. Freeman, *ibid.*, **32**, 4034 (1964).

[5] Recently A. J. Passannante, R. P. Rhodes, and L. K. Beach were issued a patent [U. S. Patent 3,347,924 (Oct 17, 1967)] for the preparation of allyl difluoramines *via* a similar reaction.

TABLE I

ALLYLIC DIFLUORAMINE CHARACTERIZATION DATA

Allylic difluoramine[a]	Bp, °C (mm)	$n^{20}D$	Yield, %	Ir spectrum, cm^{-1}	F^{19} nmr spectrum	Elemental analysis, %							
						Calcd				Found			
						C	H	F	N	C	H	F	N
$CH_2{=}CH{-}CH_2NF_2$	40–42	1.3720	69.5	1644 (C=C) 800–1000 (NF_2)	Triplet ϕ −53.7	38.71	5.37	40.86	15.05	38.52	5.41	40.80	15.47
$CH_2{=}\underset{CO_2CH_2CH_3}{\underset{\mid}{C}}{-}CH_2NF_2$	73–74 (27)	1.4085	70	1729 (C=O) 1640 (C=C) 800–1000 (NF_2)	Triplet ϕ −54.25	43.61	5.47	23.04	8.49	42.80	5.61	22.71	8.45
$CH_2{=}\underset{CN}{\underset{\mid}{C}}{-}CH_2NF_2$	54 (1.2)	1.4020	55	2205 (C≡N) 1620 (C=C) 800–1000 (NF_2)	Triplet ϕ −54.02	40.60	3.93	32.30	23.73	39.82	3.80	33.00	24.05
$CH_2{=}\underset{Br}{\underset{\mid}{C}}{-}CH_3NF_2$	36–38 (14)	...	58.5	1635 (C=C) 800–1000 (NF_2)	Triplet ϕ −53.62	20.90	2.32	22.06	8.14	20.83	2.71	21.90	8.69
$CH_3{=}\underset{CH_3}{\underset{\mid}{C}}{-}CH_2NF_2$	40–42 (19)	...	43.4	1647 (C=C) 800–1000 (NF_2)	Triplet ϕ −53.91	44.84	6.54	35.53	13.08	44.71	6.71	35.47	13.29
$CH_2{=}\underset{C_6H_5}{\underset{\mid}{C}}{-}CH_2NF_2$	60–61 (0.5)	...	62.6	1640 (C=C) 800–1000 (NF_2)	Triplet ϕ −54.63	63.91	5.32	22.48	8.28	64.11	5.62	22.33	8.09

[a] Registry no. in descending order are 16101-17-0, 16101-18-1, 16101-19-2, 16101-20-5, 16101-21-6, and 16101-22-7.

TABLE II

TRIS(DIFLUORAMINES) CHARACTERIZATION DATA

Tris(difluoramine)[a]	Bp, °C (mm)	$n^{20}D$	Yield, %	Ir spectrum, cm^{-1}	F^{19} nmr spectrum	Elemental analysis, %							
						Calcd				Found			
						C	H	F	N	C	H	F	N
$F_2NCH_2CH(NF_2)CH_2NF_2$	55–57 (55)	1.4137	45	800–1000 (NF_2)	Triplet ϕ −55.05 ($-CH_2NF_2$) Doublet ϕ −38.40 ($>CHNF_2$)	18.27	2.53	57.86	21.32	18.29	2.65	57.53	21.02
$F_2N{-}CH_2{-}\underset{CO_2CH_2CH_3}{\underset{\mid}{C}}(NF_2)CH_2NF_2$	...	...	83	1760 (C=O) 800–1000 (NF_2)	Triplet ϕ −60.0 ($-CH_2NF_2$) Collapsed quadruplet centered at ϕ −33.45 ($\leftarrow CNF_2$)	26.73	3.35	42.40	15.62	26.29	3.50	43.33	16.35
$F_2N{-}CH_3{-}\underset{CN}{\underset{\mid}{C}}(NF_2)CH_2NF_2$	...	...	57	2209 (C≡N) 800–1000 (NF_2)	Triplet ϕ −59.62 ($-CH_2NF_2$) Doublet ϕ −34.61 ($\leftarrow C{-}NF_2$)	21.53	2.26	51.10	25.11	22.03	2.39	50.70	25.31
$F_2N{-}CH_2{-}\underset{Br}{\underset{\mid}{C}}(NF_2){-}CH_3NF_2$	...	...		800–1000 (NF_2)	Triplet ϕ −56.04 ($-CH_2NF_2$) Doublet ϕ −34.86 ($\leftarrow CNF_2$)	13.04	1.45	41.30	15.22	13.19	1.63	41.13	15.65
$F_2N{-}CH_2{-}\underset{CH_3}{\underset{\mid}{C}}(NF_2)CH_2NF_2$	75–76 (6)	1.4162	87	800–1000 (NF_3)	Triplet ϕ −56.18 ($-CH_2NF_2$) Doublet ϕ −34.21 ($\leftarrow C{-}NF_2$)	22.75	3.32	54.00	19.90	23.11	3.43	53.73	19.67

[a] Registry no. in descending order are 15942-58-2, 16101-24-9, 16176-02-6, 16176-03-7, and 16101-25-0.

and **4** is unknown, since it was obtained in low yield and was never purified sufficiently well for structural characterization; however, based on available data it would appear to be compound **4**.

Tris(difluoramino)propane (**5**) results from further addition of N_2F_4 to allyldifluoramine. The major portion of the bromine liberated appears to be consumed in addition to allyl bromide to give 1,2,3-tribromopropane (**6**). Whether or not bromodifluoramine ($BrNF_2$) may be formed in the reactions and enter into the transformation is unknown. Its presence is considered unlikely since the reaction temperatures are sufficiently high to preclude its formation. In those instances where allylic iodides were employed the reactions were less complex and only the allylic or tris(difluoramines) were formed.

Similar mechanism have been proposed to describe the radical reactions of bromotrichloromethane with allyl bromide,[6] 3,3,3-trichloropropene,[7] and vinyl and perfluorovinyl compound containing allylic halogen.[8] More recently Hall[9] describes the addition of thiols to allyl chloride and bromide as proceeding *via* this mechanism. Previously, Hall and coworkers[10] explained the formation of 1,3-bis(substituted thio)-propanes by the addition of thiols to allene or to allyl sulfides in the same manner and have called the process an "allylic reversal" mechanism. Radical additions to allylically substituted olefins occurring through such "rearrangements" have been predicted by Walling.[11]

It may be noted that in these previous reports the displacement of an allylic chlorine atom from the intermediate α,α'-disubstituted radical (similar to **1**) occurs, whereas in the reaction of allyl chloride with N_2F_4 the only product formed is the normal adduct. This indicates that the NF_2 group displays a radical-leaving ability greater than the chlorine atom from the intermediate, $F_2NCH_2{-}\dot{C}H{-}CH_2Cl$, and that it exists in equilibrium with allyl chloride and $\cdot NF_2$ until coupling with a second $\cdot NF_2$ radical takes place to give the adduct. In turn the chlorine atom has a higher radical-leaving ability than either the alkylthio or trichloromethyl groups based on results from these earlier studies. Our results with the allylic bromides and iodides show that either of these groups display a greater radical-leaving character than the NF_2 group. Hence, a qualitative comparison of the stability of the groups to allylic reversal is in the order $RS \sim CCl_3 > Cl > NF_2 > Br \sim I$.

It was further demonstrated that a difluoramino radical can effect the displacement of an allylic bromine atom over a conjugated double-bond system. When 5-bromo-1,3-pentadiene was treated with N_2F_4 the products isolated were the *cis–trans* 1,2,5-tris-(difluoramino)-3-pentenes (**7**) and a bis(difluoramino) compound containing bromine. The latter product may be represented by structure **8** or **9** depending

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(6) M. S. Kharasch and M. Sage, *J. Org. Chem.*, **14**, 537 (1949).

(7) A. N. Nesmeyanov, R. K. Friedlina, and L. I. Zakharin, *Dokl. Akad. Nauk SSSR*, **81**, 199 (1951).

(8) H. Muramatsu and P. Tarrant, *J. Org. Chem.*, **29**, 1796 (1964).

(9) D. N. Hall, *ibid.*, **32**, 2082 (1967).

(10) D. N. Hall, A. A. Oswald, and K. Griesbaum, *ibid.*, **30**, 3829 (1965).

(11) C. Walling, "Molecular Rearrangements," Vol.2, P. de Mayo, Ed. Interscience Publishers, Inc., New York, N. Y., 1963, p 439.

$$CH_2{=}CHCH{=}CHCH_2Br + N_2F_4 \longrightarrow F_2NCH_2CH(NF_2)CH{=}CHCH_2NF_2 +$$

7

$$F_2NCH_2CH(NF_2)CH{=}CHCH_2Br \text{ or}$$

8

$$BrCH_2CH(NF_2)CH{=}CHCH_2NF_2$$

9

upon the mode of N_2F_4 addition, *i.e.*, 1,2 or 1,4 addition. Its structure was not definitely established. Formation of **7** can be rationalized by initial attack of a difluoramino radical at the terminal carbon atom of the conjugated double-bond system resulting in the displacement of a bromine atom and the formation of the mono(difluoramine) **10** which readily undergoes further reaction with N_2F_4 to give **7**. In this instance,

$$CH_2{=}CHCH{=}CHCH_2Br + \cdot NF_2 \longrightarrow CH_2{=}CHCH{=}CHCH_2NF_2 + \cdot Br$$

10

either 1,2 or 1,4 addition yields compound **7**. Failure to isolate **10** and the competing nature of this reaction (displacement *vs.* addition) can be explained on the basis of the enhanced rate of N_2F_4 addition to conjugated olefins over that of simple olefins.[4]

This study demonstrates the labile character of allylic bromides and iodides to attack by the difluoramino radical and offers a convenient laboratory method for the synthesis of both allylic difluoramines and tris(difluoramino)propanes. Further it suggests that other radical reagents likely would react *via* a similar mechanism to yield allylic compounds not readily obtained by other means.

The nature of the reaction of tetrafluorohydrazine with organic substrates implies that caution be exercised in the experimental work.[4] It is essential that oxygen be rigorously excluded from all reaction mixtures or explosions are apt to result. In addition care in handling of the products reported is necessary since they are impact sensitive in most instances.

Experimental Section[12]

Allyl bromide and allyl iodide were purchased from a commercial source. 2-Carboethoxyallyl bromide was prepared from the 2-carboethoxyallyl alcohol by treatment with phosphorus tribromide.[13] Other iodides were prepared by treating the corresponding bromide or chloride with sodium iodide in acetone. The tetrafluorohydrazine employed was of 95% purity containing CF compounds as the impurities. Infrared spectra were obtained with a Perkin-Elmer Infracord spectrophotometer using a sodium chloride prism while nmr spectra were obtained with a Varian Associates Model V-3000-B, high resolution spectrometer using a 40-Mc probe with trifluoroacetic acid as standard. A 0.25 in. × 5 ft column packed with dinonyl phthalate on Chromosorb in an Aerograph Model A-100-C instrument was employed at 100° for all gas chromatography work. Several examples are given to illustrate various experimental conditions.

Tetrafluorohydrazine–Allyl Iodide.—To a 100-ml, round-bottom flask fitted with magnetic stirrer was introduced 16.8 g (100 mmol) of allyl iodide and 35 ml of tetrachloroethane. The flask was connected to a glass manifold system containing a 2-l. expansion bulb and the total system deaerated by passing through three freeze–thaw cycles while under vacuum. Tetrafluorohydrazine (6.70 g, 64 mmol) was charged into the system and the mixture heated to 60° for a period of 2 hr. The pressure dropped from a maximum of 525 to 368 mm during this period. Examination of the excess gas fraction by mass spectroscopy showed that 5.63 g (54 mmol) of tetrafluorohydrazine had been consumed. The dark-colored solution was treated with mercury to remove the dissolved iodine resulting in a near-clear solution. Distillation gave 6.4 g (69.5%) of allyldifluoramine, bp 40–41°, and 1.67 g (8.4%) of 1,2,3-tris(difluoramino)propane, bp 56° (45 mm), $d^{20}{}_4$ 1.5080 as the only reaction products.

The infrared spectrum of allyldifluoramine showed weak absorption at 1644 cm^{-1} attributed to the carbon–carbon double-bond stretching vibrations and strong absorption in the 800–1000-cm^{-1} region for NF_2. Its F^{19} nmr spectrum showed only a triplet centered at ϕ −53.7 assigned to the $-CH_2NF_2$ group. The proton nmr spectrum displayed a complicated multiplet centered at τ 4.26 for the vinyl protons and a triplet (J = 29 cps) of doublets (J = 6 cps) centered at τ 5.97 indicative of the protons on the $-CH_2NF_2$ group.

1,2,3-Tris(difluoramino)propane was identified by its ir spectrum which showed strong absorption in the 800–1000-cm^{-1} region ($-NF_2$) and by its F^{19} and H^1 nmr spectra. The fluorine resonance occurred as a triplet of relative area 2 centered at ϕ −55.0 ($-CH_2NF_2$) and a doublet of relative area 1 centered at ϕ −35.9 ($-CHNF_2$). The H^1 nmr spectrum consisted of a triplet (J = 27 cps) of doublets (J = 6 cps) centered at τ 5.88. It is apparent that this resonance pattern can be assigned to the protons on the 1 and 3 positions. The major splitting into a triplet was attributed to the primary $-NF_2$ groups. Each member of the triplet was split further by the proton at the 2 position. The complex pattern which would be expected for the proton at the 2 position was not resolved.

Anal. Calcd for $C_3H_5F_2N$: C, 38.71; H, 5.38; F, 40.86; N, 15.05. Found: C, 38.52; H, 5.41; F, 40.80; N, 15.47. Calcd for $C_3H_5F_6N_3$: C, 18.27; H, 2.54; F, 57.87; N, 21.32. Found: C, 18.29; H, 2.65; F, 57.53; N, 21.02.

Tetrafluorohydrazine–Allyl Bromide.—This reaction was conveniently carried out in a flow reactor composed of feed lines for N_2F_4 and helium connected through separate calibrated flow meters into a single line to the reactor, a copper coil 0.25 in. in diameter and 12 ft in length. The allyl bromide was introduced into the feed line from a calibrated power driven syringe at a point just prior to its entrance to the reactor. The reactor was completely enclosed in an electrical furnace and the temperature measured by means of thermocouples placed within the furnace immediately adjacent to the reactor coil. The exit line from the reactor was passed through a series of cold traps cooled in the order −80, −130, and −196°. In practice, the organic materials from the reactor were always collected in the −80° trap while excess or unreacted N_2F_4 was collected in the −196° trap. The reactions were initiated by first flushing the system at a given temperature with helium and while maintaining the helium flow at the desired level both N_2F_4 and allyl bromide flows were started. For instance, at a reactor temperature of 220° and a constant helium flow of 40 cc/min, tetrafluorohydrazine was introduced at the rate of 100 cc/min and allyl bromide at the rate of 0.6 cc/min. Reaction time was 25 min at which point the flows of N_2F_4 and allyl bromide were terminated and the helium flow continued for 15 min. Contents of the −196° trap were expanded into a 2-l. bulb and examined. The mass spectrum showed the presence of N_2F_4, CF compounds (impurities in N_2F_4), SiF_4, N_2O and traces of allyl fluoride, allyldifluoramine, and allyl bromide. The −80° trap contained the major part of the organic materials. These materials were transferred from the trap into another series of cold traps at −80, −130, and −196° in order to ensure removal of any dissolved N_2F_4. After opening to the air the contents of the trap were transferred to a distillation assembly and the products isolated by distillation. From this reaction were obtained 6.61 g of allyldifluoramine, bp 40–41°, 9.07 g of allyl bromide, bp 71°, 5.75 g of a fraction, bp 37–63 (45 mm), containing the 1,2,3-tris(difluoramino)propane (identified by comparison of its glpc retention time with a pure sample) and other minor unidentified products presumably mixed bromodifluoramino compounds. From this fraction was isolated 1.67 g of 1,2,3-tribromopropane, bp 50–52° (0.4 mm). This represents approximately 50% conversion of allyl bromide into products under the described conditions and a 29% yield of allyldifluoramine. In general, allyldifluoramine was obtained in yields of 24–30% under similar conditions over a temperature range of 200–250°. Its physical properties were identical with those previously described; 1,2,3-tribromopropane was identified from its elemental analysis.

Anal. Calcd for $C_3H_5Br_3$: C, 12.83; H, 1.79; Br, 85.88. Found: C, 13.02; H, 2.04; Br, 84.80.

By altering conditions, *i.e.*, lowering the flow rates, the ratio of products could be changed to favor the formation of the tris-

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[12] All boiling points are uncorrected.

[13] S. F. Reed and M. G. Baldwin, *J. Polym. Sci., Part A-2*, 1355 (1964).

(difluoramine). For instance at flow rates of helium (10 cc/min), N$_2$F$_4$ (70 cc/min), and allyl bromide (0.1 cc/min), the tris(difluoramine) was obtained in yields of 30% compared with 4% of the allyldifluoramine.

When the reaction was conducted neat under static conditions, no allyldifluoramine could be detected. As an example, when 11.65 g (112 mmol) of tetrafluorohydrazine was added to a 1-l. stainless steel cylinder containing 12.1 g (100 mmol) of degassed allyl bromide and the mixture heated to 110° for a period of 7 hr, 4.64 g (28.5%) of 1,2,3-tris(difluoramino)propane was obtained in addition to 2.6 g (9%) of 1,2,3-tribromopropane and 3.67 g of a fraction consisting of the mixed bromodifluoramino products. This latter fraction was shown by gas chromatography to be free of both tris(difluoramino) and tribromo products, although containing other minor components, and analysis for bromine gave 59.99% (63.24% calculated for 1,2-dibromo-3-difluoraminopropane 4) while fluorine results were 19.62% (15.05% calculated for 4). In addition fluorine signals were detected in the F^{19} nmr spectrum of the crude product. Attempts to effect total purification were not successful.

Tetrafluorohydrazine–2-Carboethoxyallyl Iodide.—Into a 100-ml, round-bottom flask fitted with a magnetic stirrer was introduced a mixture of 11.3 g (50 mmol) of 2-carboethoxyallyl iodide in 25 ml of carbon tetrachloride. The flask was connected to a glass manifold system having a 2-l. expansion bulb. The solution was deaerated by passing through three freeze–thaw cycles while the system was maintained under vacuum. Tetrafluorohydrazine (12.22 g, 117 mmol) was charged into the system to give an initial pressure of 677 mm. The mixture was heated to 60° for a period of 6 hr during which time the pressure decreased to 512 mm. Analysis of the excess gas fraction indicated that 3.84 g (37 mmol) of tetrafluorohydrazine had reacted with the substrate. The reaction mixture containing solid iodine was filtered. After drying 3.9 g of iodine was obtained. The dark-colored solution was treated with mercury to remove the dissolved iodine resulting in a slightly colored solution. Carbon tetrachloride was removed at reduced pressure on a rotary evaporator and the residue distilled to give 5.78 g (70%) of 2-carboethoxyallyldifluoramine, bp 73–74° (27 mm), $n^{21}\text{D}$ 1.4085. The ir spectrum displayed absorption bands at 1729 (C═O), 1640 (C═C), and in the 800–1000-cm^{-1} region (–NF$_2$). The proton nmr spectrum showed the following signals: a triplet centered at τ 8.67 (J = 7 cps) and a quadruplet centered at τ 5.68 (J = 7 cps) typical of the CH$_3$CH$_2$– group, a triplet centered at τ 5.55 (J = 30 cps) representing protons of the –CH$_2$NF$_2$ group, and a doublet at τ 3.37 and 3.90 (J = 21 cps) for the vinyl protons. The F^{19} nmr spectra showed only a triplet centered at ϕ −54.3 attributed to the –CH$_2$NF$_2$ group.

Anal. Calcd for C$_6$H$_9$F$_2$NO$_2$: C, 43.64; H, 5.45; F, 23.03; N, 8.48. Found: C, 42.80; H, 5.61; F, 22.71; N, 8.45.

From a reaction of 2-carboethoxyallyl bromide (4.48 g, 25 mmol) and tetrafluorohydrazine (12.72 g, 122 mmol) conducted in 25 ml of chlorobenzene under similar conditions was isolated 1.63 g (39%) of 2-carboethoxyallyldifluoramine from a mixture of other unidentified products. This product was identical in every respect with that isolated from the iodide reaction.

Tetrafluorohydrazine–2-Carboethoxyallyldifluoramine.—A solution of 2.07 g (12.5 mmol) of 2-carboethoxyallyldifluoramine in 30 ml of carbon tetrachloride was introduced into a thick-walled glass container (aerosol tube, 100-ml capacity) and the tube connected to a high-pressure stainless steel manifold. The solution was deaerated by flushing thoroughly with nitrogen and the nitrogen removed under vacuum. Tetrafluorohydrazine was then added to give an equilibrium pressure of 70 psi. The mixture was heated to 90° for a period of 5 hr during which time the tetrafluorohydrazine pressure was maintained between 81 and 49 psi by recharging the system as necessary. After cooling, the excess tetrafluorohydrazine was vented and the solution flushed thoroughly with nitrogen. Finally, the tube was opened to the air and removed from the manifold. The solvent was removed at reduced pressure on a rotary evaporator to give 2.8 g (83%) of 1,2,3-tris(difluoramino)-2-carboethoxypropane identified by its ir spectrum which showed strong carbonyl absorption at 1760 cm^{-1} and NF absorption in the 900–1000-cm^{-1} region. Its F^{19} nmr spectrum displayed a triplet centered at ϕ −60.01 (–CH$_2$-NF$_2$) and a collapsed quadruplet centered at ϕ −33.45 ($\geqslant$C–NF$_2$). The ratio of the peak area in the triplet to that of the collapsed quadruplet was approximately 2:1. The proton nmr spectrum displayed signals for the ethyl group as a triplet (–CH$_3$) centered at τ 8.62 (J = 6 cps) and a quadruplet (–CH$_2$–) centered at 5.57 (J = 8 cps). The protons of the –CH$_2$NF$_2$ groups appeared as a triplet centered at 5.65 (J = 27 cps).

Anal. Calcd for C$_6$H$_9$F$_6$N$_3$O$_2$: C, 26.77; H, 3.35; F, 42.38; N, 15.61. Fond: C, 26.29; H, 3.50; F, 43.33; N, 16.35.

Tetrafluorohydrazine–2-Cyanoallyl Iodide.—A solution of 24.0 g (0.12 mol) of 2-cyanoallyl iodide in 35 ml of carbon tetrachloride was introduced into a 100-ml round-bottom flask which was then connected to a glass manifold having a 2-l. expansion bulb. The mixture was deaerated by passing through three freeze–thaw cycles while the system was maintained under vacuum. Eighty mmoles (8.34 g) of tetrafluorohydrazine was added to give an initial pressure of 570 mm. The flask was then heated to 55–60° for a period of 12 hr during which time the pressure dropped to 125 mm. Analysis of the excess gas fraction indicated that 50 mmol of tetrafluorohydrazine (94%) had reacted based on formation of the 2-cyanoallyldifluoramine. The reaction mixture contained solid iodine which was removed by filtration, dried, and weighed. A total of 10.4 g (68%) of iodine was recovered. The dark-colored mixture was treated with mercury for several hours to remove the dissolved iodine resulting in a slightly colored transparent solution.

After removal of carbon tetrachloride the residue was distilled to give 4.87 g (55.5%) of 2-cyanoallyldifluoramine, bp 54° (1.2 mm), $n^{19.5}\text{D}$ 1.4020. The ir spectrum showed absorption bands at 2205 (C≡N), 1620 (C═C), and 900–1000 cm^{-1} (NF$_2$). The fluorine nmr spectrum showed a triplet centered at ϕ −54.02 typical of the –CH$_2$NF$_2$ group. The proton nmr spectrum showed a doublet at τ 3.70 and 3.80 for the vinyl protons and a triplet centered at 5.25 (J = 28 cps) for the protons of the –CH$_2$NF$_2$ group.

Anal. Calcd for C$_4$H$_4$F$_2$N$_2$: C, 40.68; H, 3.39; F, 32.20; N, 23.73. Found: C, 39.82; H, 3.80; F, 33.00; N, 24.05.

Tetrafluorohydrazine–2-Cyanoallyldifluoramine.—A mixture of 2.0 g (16.9 mmol) of 2-cyanoallyldifluoramine in 30 ml of carbon tetrachloride was introduced into a glass aerosol tube (100-ml capacity), and the tube was connected to a high-pressure stainless steel manifold. The solution was deaerated with nitrogen and the nitrogen removed under vacuum. The system was then charged with tetrafluorohydrazine to an equilibrium pressure of 75 psi at 35°. Heating was continued at 95–100° over a period of 1.5 hr during which time the pressure was maintained between 39–75 psi by recharging with tetrafluorohydrazine as necessary. After cooling, the excess tetrafluorohydrazine was vented and the solution degassed by bubbling nitrogen through it followed by an application of a vacuum. The tube was then opened to the air and removed from the manifold. The solvent was removed at reduced pressure on a rotary evaporator to give 2.36 g of a liquid residue showing weak ir absorption at 2209 cm^{-1} (–C≡N) and strong absorption in the 800–1000-cm^{-1} region (–NF$_2$). Preliminary impact sensitivity test indicated the liquid to be relatively sensitive; hence, no attempt was made toward its purification. However, it was examined by gas chromatography and found to be 95% pure. Its identity as 1,2,3-tris(difluoramino)-2-cyanopropane (62%) was finally based on the elemental analysis.

Anal. Calcd for C$_4$H$_4$F$_6$N$_4$: C, 21.62; H, 1.80; F, 51.35; N, 25.23. Found: C, 22.03; H, 2.39; F, 50.20; N, 25.31.

Tetrafluorohydrazine–5-Bromo-1,3-pentadiene.—Following the usual preparative procedure a solution of 3.62 g (24.9 mmol) of 5-bromo-1,3-pentadiene in 25 ml of chlorobenzene was treated with 6.24 g (60 mmol) of N$_2$F$_4$ (maximum pressure 703 psi) at 65° for a period of 2.5 hr. All NF-containing materials were separated from the solvent by distillation, bp 41–80° (30 mm). Gas chromatography was employed to separate the three major products in sufficient quantity for analysis.

One isomer of 1,2,5-tris(difluoramino)-3-pentene was characterized by its F^{19} nmr spectrum which displayed two triplets centered at ϕ −53.56 and −52.09, and a singlet at −46.96. The peak areas were approximately equal. The other minor isomer was never obtained in sufficient purity for complete structural analysis since it was not free of the above isomer. As a mixture where it was the predominant component, it displayed signals in the F^{19} nmr spectrum as two triplets at ϕ −54.37 and −53.04 and a singlet at −47.70.

Anal. Calcd for C$_5$H$_7$F$_6$N$_3$: C, 26.88; H, 3.14; F, 51.20; N, 18.83. Found (pure isomer): C, 26.59; H, 3.28; F, 51.75; N, 19.24. Found (isomer mixture): C, 26.72; H, 3.21; F, 51.51; N, 19.02.

The bis(difluoramino) compound obtained in the above reaction was characterized only by its elemental analysis which indicated a normal adduct of the pentadienyl bromide.

Anal. Calcd for $C_5H_7BrF_4N_2$: C, 23.94; H, 2.79; Br, 31.87; F, 30.27; N, 11.15. Found: C, 23.76; H, 2.59; Br, 31.54; F, 30.40; N, 11.37.

Registry No.—Tetrafluorohydrazine, 10,036-47-2; **6**, 96-11-7; *cis* **7**, 16101-27-2; *trans* **7**, 16101-28-3.

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Radiation-Induced Hydroxylation of Nitrobenzene in Dilute Aqueous Solution[1]

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The isomeric nitrophenols have been quantitatively determined by gas–liquid partition chromatography in irradiated solutions of dilute aqueous nitrobenzene. The relative rates of hydroxylation for $C_6H_5NO_2$ and $C_6D_5NO_2$ have been found to be identical and therefore the initial step of hydroxylation is the addition of ·OH to the aromatic ring The *G* values obtained for nitrophenols suggest preferential dimer formation. If the solvated electrons are not completely scavenged additional nitrophenols are produced by a complicated set of reactions involving the nitro-substituted hydroxycyclohexadienyl radical, the dimers, and their subsequent products. The mechanisms for these processes are discussed.

Aromatic compounds are easily and often selectively hydroxylated in nature by enzymes[2] whereas hydroxylation by chemical reagents is difficult and the mechanisms are complex.[3] Radiation-induced hydroxylation offers a somewhat simpler system since, in this case, the generation of hydroxyl radicals *in situ* avoids the necessity of adding an additional reagent to the system. The hydroxyl radical together with the solvated electron, hydrogen atom, hydrogen molecule, and hydrogen peroxide are the chemical species primarily formed by γ irradiation of water.[4,5] We have undertaken a systematic investigation of the radiation induced hydroxylation of monosubstituted aromatic compounds in dilute aqueous solutions. Our primary concern was to obtain meaningful data for isomeric distributions and partial rate factors, and to compare chemical and radiation-induced hydroxylations. We examined initially the effect of irradiation by γ rays on nitrobenzene in dilute aqueous solutions. In the course of our work it became apparent that the radiation chemistry of this system is somewhat more complicated than we anticipated. For this reason we are reporting the hydroxylation of nitrobenzene separately.

Experimental Section

Two separate cobalt-60 γ-irradiation facilities were used. The absorbed dose rates were determined to be 20.8×10^2 and 3.45×10^2 rads min^{-1} by the Fricke dosimeter taking $G(Fe^{3+}) = 15.5$.[6]

For the irradiation of air-saturated solution redistilled reagent grade nitrobenzene was dissolved in triply distilled water by vigorous shaking and its concentration was determined spectrophotometrically at 269 mμ.[7] The pH of the triply distilled water was adjusted by the addition of small volumes of concentrated sulfuric acid or sodium hydroxide to the required value. Argon, oxygen, and nitrous oxide saturated solutions were prepared by bubbling the high purity gas through the triply distilled water in the irradiation cell. The gas was introduced into the irradiation cell by the use of a hypodermic needle which was punched through a silicone septum and pushed close to the bottom of the cell. An outlet for the saturating gas was provided by inserting another needle through a second septum above the water level. The duration of the saturation was about 15–20 min and it was enhanced by frequent shaking. After saturation the needles were withdrawn and the required amount of nitrobenzene was introduced with a Hamilton gas-tight syringe and dissolved by vigrous shaking.

Deuterated nitrobenzene, $C_6D_5NO_2$, was obtained from Mallinckrodt Nuclear Corp. and its deuterium content was established to be 98% by mass spectroscopy.[8]

The conversion of nitrobenzene into products was kept at less than 1% to avoid secondary reactions. After the completion of irradiation a small portion of the solution (usually 10 ml) was analyzed for nitrite, nitrate, and hydrogen peroxide and the remainder (150 ml) was treated for nitrophenols and phenol.

Nitrite was analyzed by the Griess–Ilosvay test[9] and the nitrate was determined by the brucine method.[9] Standard sodium nitrate solutions were used to construct calibration curves.

Hydrogen peroxide was analyzed spectrophotometrically by the iodide method;[10] calibration curves were constructed using dilutions of stock solutions of hydrogen peroxide whose concentrations were standardized by B. D. H. standard ceric sulfate solution.[11] The irradiated solution, without the added reagents, was used as a blank for the spectroscopic determinations.

After adjusting the pH of the aqueous irradiated nitrobenzene solutions to 12.5 with sodium hydroxide, the solution was extracted with ether to remove the unreacted nitrobenzene. The pH of the aqueous layer was readjusted to 2.0 with HCl and was extracted twice with 100-ml portions of redistilled ether. These ether layers were concentrated by rotary evaporation to 5.0 ml at temperatures not exceeding 20° and were analyzed by gas–liquid partition chromatography. Using a 1-m glass column [0.25 i.d. packed with 2% Versamid 900 (F & M) on Chromasorb W] with temperature programming at 2.5°/min from 25° and at a flow rate of 115 cc of He/min,[12] the following retention times (in minutes) were obtained: *o*-nitrophenol, 30; phenol, 42; *m*-nitrophenol, 57; and *p*-nitrophenol, 62. Using the same column [but packed with a mixture of 2% Versamid on Chromosorb W (75%) and 1% 1,2,3,4-tetrakis(2-cyanoethoxy)butane on C-22 (25%)], the same temperature programming, and an identical He flow rate, the following retention times (in minutes)

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[1] Supported in part by the U. S. Atomic Energy Commission.

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[4] The yields of these species at pH 7 are[5] $G_{OH} = 2.4$; $G_{e_{aq}^-} = 2.8 \pm 0.2$; $G_H = 0.6$; $G_{H_2} = 0.5$; $G_{H_2O_2} = 0.7$.

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[8] We are indebted to Mr. G. Buzzard for this determination.

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