

The hydrolysis procedure was adapted from Vliet, Marvel, and Hsueh.¹³ A mixture of 7.5 g of the above ester and 7.5 g of potassium hydroxide in 10 ml of water was refluxed gently for 2 hr. An additional 10 ml of water was added and ethanol was distilled. The mixture was then refluxed with aqueous sulfuric acid and extracted with ether. The washed and dried extract was distilled, benzene was added and distilled off, and the residue was distilled through a small column yielding 2.4 g (60%) of caproic- β -*d* acid, bp 97–98° (6–7 mm), α_D^{25} $-0.055 \pm 0.009^\circ$ (*l* 1).

Butanol-1-*d* having $\alpha_D +0.076 \pm 0.005^\circ$ (*l* 2, 25 atom % D) was carried through this same sequence to prepare caproic- β -*d* acid, $\alpha_D -0.030 \pm 0.002^\circ$ (*l* 1).¹⁴

1-Bromopentane-2-*d*.—The procedure was adapted from Cristol and Firth.⁷ A slurry of 6.1 g of red mercuric oxide and 4.2 g of the caproic- β -*d* acid, $\alpha_D -0.041 \pm 0.008^\circ$ (*l* 1), in 50 ml of dry carbon tetrachloride was protected from light and refluxed with 2 ml of bromine in 10 ml of carbon tetrachloride for 1 hr. The mixture was poured into dilute sodium hydroxide and filtered through a Super Cel mat. The washed and dried organic layer was distilled through a small column giving crude 1-bromopentane-2-*d* which was purified on a glpc column yielding 2.6 g (47%), $\alpha_D^{25} -0.452 \pm 0.007^\circ$ (*l* 1).

In the preliminary experiments,¹⁴ caproic- β -*d* acid, $\alpha_D -0.030^\circ$, (*l* 1) gave 1-bromopentane-2-*d* having $\alpha_D -0.359 \pm 0.003^\circ$ (*l* 1).

1-Pentene-2-*d*.—Methyl valerate (79 g, 0.68 mole) was refluxed overnight with 100 g (3.3 moles) of methanol-*d*,¹⁵ in which 0.4 g of sodium had been dissolved. The mixture was diluted with dilute hydrochloric acid and ice and extracted with ether. Distillation of the washed and dried extract gave an 85% recovery of the ester. The treatment was repeated until the nmr spectrum showed the absence of α protons. The methyl valerate- α -*d*₂ was reduced with lithium aluminum hydride in ether in the usual way to give 1-pentanol-2-*d*₂; this alcohol was treated with equivalent amounts of acetyl chloride and pyridine to give 1-pentyl-2-*d*₂ acetate, bp 146–147°. This ester was pyrolyzed by dropping through a Vicor tube packed with glass helices and heated to 550°. From 10 g of ester there was obtained 3 g of recovered ester and 3 g of 1-pentene-2-*d* whose nmr spectrum showed one deuterium atom.

Pentane-2-*d* from 1-Pentene-2-*d*.—To a mixture of 47.7 g (0.35 mole) of α -pinene ($[\alpha]_D +38.75^\circ$, 75.8% optically pure) and 4.97 g (0.131 mole) of sodium borohydride in 225 ml of

freshly distilled diglyme maintained at 0° was added 48.8 ml (0.175 mole) of boron fluoride diglymate. After several hours at 0°, 7 g of 1-pentene-2-*d* in diglyme was added. The mixture was maintained at 0° for 2 hr and stirred at room temperature for 8 hr. After decomposition of excess hydride with ethylene glycol, 45 ml of glacial acetic acid was added and the mixture was stirred for 2 hr. Distillation gave pentane-2-*d* which was purified by bulb-to-bulb distillation; gc showed the absence of pinene but the infrared showed the presence of a small amount of acetic acid. Measurement of rotation gave $\alpha_D^{25} -0.12 \pm 0.01^\circ$ (*l* 1), $[\alpha]_D^{25} -0.19^\circ$.

1-Pentanol-2-*d*.—The preceding hydroboration preparation was followed except that decomposition of the organoborane was accomplished with 50 ml of 30% hydrogen peroxide. Extraction with ether and distillation gave 1-pentanol-2-*d* whose gc showed contamination by pinene and other impurities. Purification by chromatography on silica gel and gc (Carbowax) gave 0.9 g of product having a C-D band at 2120 cm^{-1} and $\alpha_{546} -0.205^\circ$, $\alpha_{578} -0.190^\circ$ (*l* 1) ($[\alpha]_D -0.22 \pm 0.01^\circ$).

1-Bromopentane-2-*d* from 1-Pentanol-2-*d*.—The deuterio alcohol was diluted with two parts of 1-pentanol prepared by reduction of valeric acid with lithium aluminum hydride. The total of 3 cc was warmed with 5 g of phosphorus tribromide. After addition of water the amyl bromide layer was separated, washed, dried, and distilled giving 62% of product, bp 126–127°, 99.9% pure by glpc. The C-D band was at 2130 cm^{-1} ; $\alpha_{546} -0.343^\circ$, $\alpha_{578} -0.300^\circ$ (*l* 1) ($[\alpha]_D -0.245^\circ$). Correcting for fully deuterated material gives $[\alpha]_D -0.74 \pm 0.02^\circ$.

Pentane-2-*d* from 1-Pentene.—To a solution of 1.5 g (0.036 mole) of lithium aluminum deuteride and 13.1 g (0.096 mole) of α -pinene (pure by glpc, $[\alpha]_D^{25} +45.9^\circ$, 90% optically pure) in diglyme was added 14 ml (0.048 mole) of boron fluoride diglymate. After several hours at 5–10°, the mixture was cooled to 0° and 3.2 g (0.046 mole) of 1-pentene was added. After stirring overnight the mixture was decomposed first with ethylene glycol followed by glacial acetic acid. Distillation and redistillation gave 1.0 ml of product which was further purified by washing with cold concentrated H₂SO₄ and finally by glpc (PBG). The pentane-2-*d* showed a C-D band at 2145 cm^{-1} and 0.70 ± 0.05 atom of deuterium per molecule in the nmr.

The ORD curve taken on a Cary 60 spectropolarimeter gave a normal Drude plot with λ_0 155 μm and $[\alpha]_D^{25} +0.158^\circ$.

Registry No.—(S)-(+)-1-Butanol-1-*d*, 10035-71-9; *p*-nitrobenzenesulfonate, 10035-72-0; diethyl (butyl-1-*d*)-malonate, 10035-73-1; caproic- β -*d* acid, 10035-74-2; 1-bromopentane-2-*d*, 10035-75-3; 1-pentyl-2-*d*₂ acetate, 10035-76-4; 1-pentanol-2-*d*, 10035-77-5; pentane-2-*d*, 10035-83-3.

(13) E. B. Vliet, C. S. Marvel, and C. M. Hsueh, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 416.

(14) These preliminary experiments were performed by V. Sarich.

(15) A. Streitwieser, Jr., L. Verbit, and P. Stang, *J. Org. Chem.*, **29**, 3706 (1964).

Radical Reactions of Tetrafluorohydrazine. IV. Addition to Acetylenes^{1a}

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Tetrafluorohydrazine reacts with acetylenes to produce α -fluoro- α -difluoramino fluorimines. These products appear to be produced by rearrangement of the original adduct, the α,β -bis(difluoramino)ethylenes.

Following the discovery that tetrafluorohydrazine (N₂F₄) reacts smoothly with a wide variety of olefins to produce the corresponding vicinal bis(difluoramines),^{2,3} the behavior of acetylenes in this reaction

(1) (a) This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Alabama under Contract Numbers DA-01-021 ORD-5135 (1959) and DA-01-021 AMC-11536(Z). (b) Deceased. (c) To whom correspondence should be directed.

(2) R. C. Petry and J. P. Freeman, Abstract S-46, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

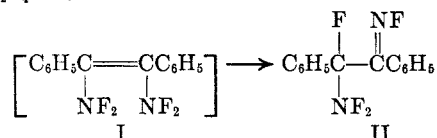
(3) A. J. Dijkstra, J. A. Kerr, and A. F. Trotman-Dickinson, *J. Chem. Soc., Sec. A*, 582 (1966). For leading references and pertinent work, see A. L. Logothetis, *J. Org. Chem.*, **31**, 3686 (1966); A. L. Logothetis and G. N. Sausen, *ibid.*, **31**, 3689 (1966).

was examined. Two objectives were involved: the synthesis of vinyl difluoramines and of tetrakis(difluoramines). However, a brief examination of this reaction revealed the instability of vinyl difluoramines which precluded the further addition of N₂F₄.

Tolane, acetylenedicarboxylic ester, and isopropenyl acetylene were investigated. Allene was also studied briefly and, since it yielded products analogous to those derived from acetylenes, its reaction will be described. Finally, β -bromostyrene reacted with N₂F₄ to produce a product related to acetylene addition products. In general, it was found that the reaction of acetylenes

and N_2F_4 was complex in contrast to the olefin addition² and usually large quantities of nitrogen and silicon tetrafluoride were observed among the products. No useful materials could be isolated from acetylene itself; better results were obtained from higher molecular weight acetylenes.

Tolane and N_2F_4 reacted smoothly when heated in methylene chloride solution under pressure. The product had the correct elemental analysis for the mono-addition product but its F^{19} nuclear magnetic resonance (nmr) spectrum established that it was not the expected adduct I but a rearrangement product, 1-fluoro-1-difluoramino-2-fluorimino-1,2-diphenylethane (II). The



F^{19} nmr spectrum of this readily purified compound was analyzed in some detail and should serve as a model for this type of compound.

The F^{19} nmr spectrum of II is clearly of the ABMX type in conventional notation,⁴ with the NF_2 fluorines being the strongly coupled set. No N^{14} couplings are obvious; apparently the quadrupole relaxation effectively decouples N^{14} , although a pronounced broadness of the spectral peaks (2–4 cps) is an indication of the existence of N^{14} nuclei in the system.

The F^{19} resonance of the difluoramino group is a complicated set of peaks near $\phi -23$. The two fluorines are magnetically nonequivalent as a result of the attachment of the difluoramino group to an asymmetric carbon,⁵ but they are not greatly shifted from one another, F_A being at $\phi -27.08$ and F_B at $\phi -19.58$. These two fluorines are strongly coupled ($J_{AB} = 570$ cps), so that the gross appearance of the NF_2 spectrum is that of an AB system. The downfield fluorine appears to be coupled to both the CF and $C=NF$ groups. While accurate coupling constants cannot be measured directly in patterns which include AB behavior, spin-spin decoupling experiments indicate that the coupling constant of F_A to CF is 8.0 cps; that of F_A to $C=NF$, 5.0 cps. The upfield fluorine F_B appears to be coupled to the CF with $J = 8.0$ cps; the coupling of F_B to the fluorimino fluorine appears to be quite small (<1 cps), since neither set of peaks shows much change upon attempted decoupling.

The fluorimino peak at $\phi -38.3$ is a broad singlet which shows little distinguishable coupling. Decoupling of NF_2 , however, shows a doublet due to a 4.0-cps coupling to the CF. The couplings to the F_A and F_B fluorines of the NF_2 appear to be about 5 cps and less than 1 cps, respectively. Part of the lack of clarity of this pattern is due to its X nature.

The CF resonance located at $\phi +158.2$ can be interpreted as the X portion of an ABMX spectrum. The couplings of both NF_2 fluorine nuclei appear to

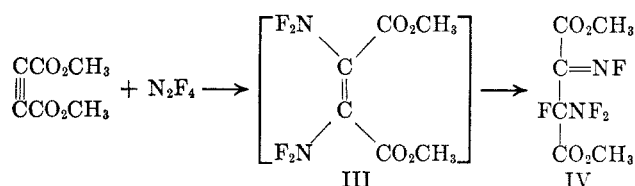
(4) J. Pople, W. Schneider, and H. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., p 98 ff.

(5) The AB spectrum implies that the inversion of the nitrogen is not occurring rapidly enough to equalize the F^{19} shifts. This behavior is unexpected in view of other NRR'R'' systems. D. Griffiths and J. D. Roberts *J. Am. Chem. Soc.*, **87**, 4089 (1965). For a detailed discussion of the spectra of *meso* and *dl*- α,α -bis(difluoramino)bibenzyls, see F. A. Johnson, C. Haney, and T. E. Stevens, *J. Org. Chem.*, **32**, 466 (1967).

be about 8 cps; the extreme AB nature and large J_{AB} of the NF_2 group causes the CF resonance (decoupled from $C=NF$) to appear as a deceptively simple 1:2:1 triplet, although the center line is in fact an accidental superposition⁶ of lines 10 and 11 of the X portion. Undecoupled, the CF appears as a triplet of doublets ($J = 4$ cps) from the influence of the fluorimino group.

Excellent agreement was found between the experimental spectrum and a spectrum calculated with the Swalen-Reilly program⁷ using the above constants.

Tetrafluorohydrazine reacted with dimethyl acetylenedicarboxylate in tetrachloroethane at 120° under pressure. The reaction was more sluggish than with aliphatic olefins and much decomposition occurred as evidenced by the presence of nitrogen and tarry residue following the reaction. The main product⁸ isolated was not the adduct III but the rearrangement product IV.



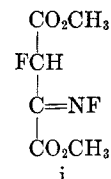
The F^{19} nmr spectrum of this product consisted of signals at $\phi -47.4$, -23.8 , and $+159.2$ in the ratio of 1:2:1. The low field signals were broad and unresolved and the high field signal appeared to be a poorly resolved triplet. This spectrum is consistent with structure IV, the high field signal being due to the CF group coupled to the difluoramino group. The chemical shift of the difluoramino group also is indicative of its attachment to a carbon bearing a fluorine atom.⁹ While this spectrum was not analyzed with the same thoroughness as that from the tolane adduct, its general features are very similar to that spectrum.

Isopropenylacetylene reacted smoothly with N_2F_4 to produce a mixture of olefin adduct V and rearranged 1,4 adduct VI; adduct VI, a 1:1 mixture of *cis* and *trans* olefins by nmr, predominated about 3:1 over V. The evidence for structures V and VI is summarized in the Experimental Section.¹⁰ Dehydrofluorination of

(6) K. Wiberg and B. Nist, "Interpretation of the NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, p 21.

(7) J. O. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

(8) A second product isolated in low yield appeared to possess structure i. Its F^{19} nmr spectrum showed bands of equal area at $\phi -42.3$ (doublet)

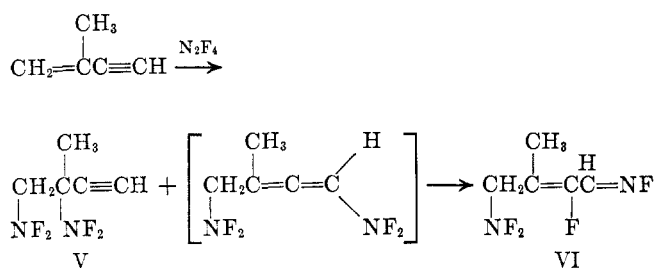


and $+195.8$ (doublet of doublets). Its proton nmr spectrum consisted of a broadened doublet at $\tau 4.4$ ($J = 40$ cps) due to one hydrogen in addition to the ester methyl bands centering at $\tau 6.3$. This product probably derives from hydrogen abstraction from the solvent by the originally formed difluoroaminovinyl radical followed by the fluorotropic shift.

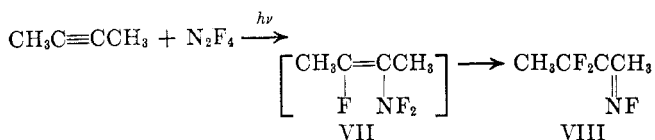
(9) F. A. Johnson, to be published.

(10) The assumption is made that in the fluorimine function, $CH=NF$, the proton and fluorine atoms are *cis*. The observed J_{HF} values of 64 and 67 cps for this group in the isomers of VI correspond closely to that observed (71 cps) in *cis*-benzaldehydofluorimine (W. H. Graham, unpublished observation). Also, elimination of HF from aldehydofluorimines of the *trans* configuration may be too facile to allow their easy isolation; certainly few examples of these compounds have been obtained.

VI produced a mixture of *cis*- and *trans*-1,2-dicyano-1-fluoro-1-propene.

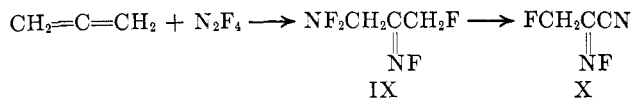


Since no α,β -bis(difluoramino)ethylenes were isolated here, it can only be postulated that an intermediate such as I or III rearranges to α -difluoramino- α -fluoro fluorimines. Two apparent examples of vinyl difluoramino rearrangements have been reported.¹¹ For example, irradiation of tetrafluorohydrazine and 2-butyne gave an addition compound VIII that most likely arose from VII.



Certainly vinyl difluoramines are logical intermediates in these reactions, and it seems reasonable that the driving force for this rearrangement involves the thermodynamic stability of CF compared with NF bonds and C=N compared with C=C bonds. Whether the reaction is inter- or intramolecular and whether it is radical, ionic, or four center is completely unknown.

Allene was examined in this reaction since it was expected that a similar rearrangement would follow the addition. In fact these expectations were fulfilled although the reaction was complicated by extensive dehydrofluorination as the reaction product attacked glass containers. The F^{19} nmr spectrum of the product revealed the presence of the rearranged adduct IX along with variable amounts of its decomposition product X. The instability of a CH_2NF_2 linkage adja-

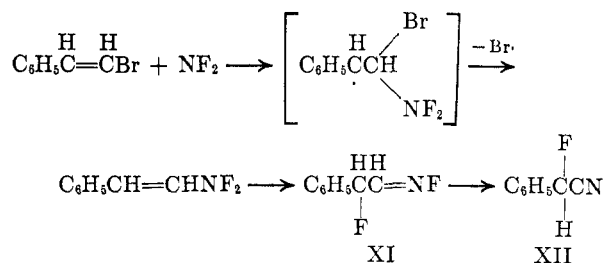


cent to carbon-oxygen or carbon-nitrogen multiple bonds was noted previously.² The presence of X was inferred from the infrared and nmr spectra but a pure sample was not isolated.

A similar rearrangement was observed in the addition of N_2F_4 to β -bromostyrene. In this case addition of the difluoramino radicals is apparently followed at least in the early stages of the reaction by loss of bromine to produce β -difluoramino styrene which then undergoes rearrangement to yield XI and finally the nitrile XII. The fluorimine XI appeared to be present in the crude product, but on handling it was converted into XII. Some dibromomonodifluoramino-1-phenylethane also was isolated.¹²

(11) (a) C. L. Bumgardner, *Tetrahedron Letters*, 3683 (1964); (b) A. L. Logothesis, *J. Org. Chem.*, **31**, 3686 (1966).

(12) A similar reaction was noted in the addition of N_2O_4 to β -bromostyrene to produce β -nitrostyrene. T. E. Stevens, *ibid.*, **25**, 1658 (1960). A dibromomononitrophenylethane was isolated here.



Experimental Section

Caution.—Mixtures of tetrafluorohydrazine, organic compounds and oxygen are highly explosive. All reactions involving tetrafluorohydrazine should be conducted with adequate precautions.

Reaction of Diphenylacetylene and Tetrafluorohydrazine.—A solution of 5.0 g of diphenylacetylene in 50 ml of methylene chloride was warmed to 80° in a Fischer-Porter pressure tube under pressure of excess tetrafluorohydrazine. After 3 hr at 80° the excess tetrafluorohydrazine was vented and the solution was flushed well with nitrogen. The methylene chloride was removed at reduced pressure, and the residue was taken up in pentane-methylene chloride (10:1) and chromatographed on silica gel. Elution of the column with the same solvent gave 0.22 g of recovered diphenylacetylene; elution with pentane-methylene chloride gave 1-fluoro-1-difluoroamino-2-fluorimino-1,2-diphenylethane, 4.07 g (52%), a pale yellow liquid.

Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{F}_4\text{N}_2$: C, 59.47; H, 3.57; F, 26.9; N, 9.93. Found: C, 59.55; H, 3.89; F, 26.5; N, 10.71.

Dimethyl Acetylenedicarboxylate and Tetrafluorohydrazine.—A mixture of 5.0 g (0.035 mole) of the ester, 0.042 mole of N_2F_4 , and 52 ml of tetrachloroethane was heated to 120° for 24 hr. After removal of the gaseous products and solvent a liquid residue was obtained which was distilled to yield 1.6 g of dimethyl α -fluoro- α -difluoramino- β -fluoriminosuccinate (IV), bp 45–56° (0.6 mm).

Anal. Calcd for $\text{C}_6\text{H}_8\text{F}_4\text{N}_2\text{O}_4$: C, 29.28; H, 2.46; N, 11.38. Found: C, 30.09; H, 2.80; N, 10.46.

Further distillation yielded 0.4 g of a liquid believed to be dimethyl α -fluoro- β -fluoriminosuccinate (I), bp 46° (0.03 mm).

Anal. Calcd for $\text{C}_6\text{H}_7\text{F}_2\text{NO}_4$: C, 36.9; H, 3.6; N, 7.2. Found: C, 34.5; H, 3.4; N, 7.8.

Isopropenylacetylene and Tetrafluorohydrazine.—A mixture of 4.2 g (0.064 mole) of isopropenylacetylene and 2.9 (0.13 mole) of N_2F_4 was heated in a 1-l. stainless-steel bomb for 2 hr at 70°. The bomb was cooled to –78° and the gaseous products were removed by distillation. The product was removed from the bomb in methylene chloride solution. The liquid product was then distilled in a short Vigreux column.

The first fraction, bp 32–33° (30 mm), was identified as 3,4-bis(difluoramino)-3-methyl-1-butyne (V). The infrared spectrum showed $\text{C}\equiv\text{CH}$ absorption at 3.05 μ , $\text{C}\equiv\text{C}$ at 4.70 μ , NF at 11.05 and 11.03 μ .

Anal. Calcd for $\text{C}_6\text{H}_8\text{N}_2\text{F}_4$: C, 35.30; H, 3.56; N, 16.47. Found: C, 35.51; H, 4.03; N, 16.47.

The F^{19} nmr spectrum of V contained a triplet, $J_{\text{HF}} = 24$ cps, at $\phi - 62.0$ (CH_2NF_2) and a broad peak at $\phi - 34.2$ (tertiary NF_2).

The second fraction, bp 45° (3 mm), appeared to be a mixture of *cis*- and *trans*-1-fluorimino-4-difluoramino-2-fluoro-3-methylbutene-2 (VI). The infrared spectrum showed C=N absorption at 5.96 μ and C=C absorption at 6.31 μ .

Anal. Calcd for $\text{C}_8\text{H}_8\text{N}_2\text{F}_4$: F, 44.7; C, 35.30; H, 3.56; N, 16.47. Found: F, 44.3; C, 35.50; H, 3.79; N, 16.58.

One isomer of VI had F^{19} nmr peaks at $\phi - 55.6$, triplet, $J_{\text{HF}} = 28$ cps (CH_2NF_2), at $\phi - 44.6$, doublet, $J_{\text{HF}} = 67$ cps ($\text{C}=\text{NF}$), and at $\phi + 120.8$, $J_{\text{HF}} = 18$ cps (CF). The corresponding peaks in the other isomer were at $\phi - 54.4$, $J_{\text{HF}} = 28$ cps, $\phi - 43.8$, $J_{\text{HF}} = 64$ cps, and $\phi + 116.2$, $J_{\text{HF}} = 18$ cps.

The proton nmr spectrum of the mixture of isomers had the CH_3 as a multiplet at τ 7.98, the CH_2NF_2 triplet, $J_{\text{HF}} = 28$ cps, at τ 5.74, and the $\text{CH}=\text{NF}$ protons each centered near τ 1.68. Each was a doublet of doublets, $J_{\text{HNF}} = 67$ and 64 cps.

Reaction of N_2F_4 and β -Bromostyrene.—A mixture of 3.0 g of β -bromostyrene and 30 ml of methylene chloride was exposed to N_2F_4 under pressure at 35° for 3 hr. The F^{19} nmr spectrum of the crude product indicated four major fluorine-containing

groups: a CF doublet at $\phi +170.8$, $J_{HF} = 48$ cps, due to nitrile XII, an NF doublet at $\phi -53.0$, $J_{HF} =$ about 66 cps, and a CF doublet, $J_{HF} = 48$ cps, of triplets, $J_{HF} = 4$ cps, at $\phi +183.7$ due to fluorimine XI, and a doublet, $J_{HNF} = 24$ cps, at $\phi -44.8$ due to the dibromo(difluoramino)phenylethane. With time, the 53.0 and $\phi +183.7$ peaks disappeared and the $\phi +170.8$ peak grew. Chromatography of the crude residue on silica gel packed with pentane gave, in the pentane-methylene chloride (10:1) eluent, the dibromodifluoraminoethane whose F^{19} nmr spectrum is described above. It was a colorless liquid.

Anal. Calcd for $C_8H_8BrNF_2$: C, 30.50; H, 2.24; N, 4.44. Found: C, 30.39; H, 2.30; N, 4.47.

From the pentane-methylene chloride (2:1) eluent was obtained α -fluorophenylacetonitrile, a colorless liquid, F^{19} nmr discussed above.

Anal. Calcd for C_8H_8NF : C, 71.10; H, 4.48; N, 10.36. Found: C, 71.46; H, 4.59; N, 10.59.

1,2-Dicyano-1-fluoro-1-propene.—A solution of 2 g of 1-fluorimino-4-difluoramino-2-fluoro-3-methyl-2-butene in 20 ml of methylene chloride was cooled in an ice bath while 5 ml of triethylamine in 20 ml of methylene chloride was added dropwise. After 1 hr at 20°, the solution was washed with water, 10%

aqueous hydrochloric acid, and water. The methylene chloride solution was distilled *in vacuo* through traps cooled to 0 and -80° . The 0° trap retained the 1,2-dicyano-1-fluoro-1-propene; two peaks (*cis,trans* isomers) were present in glpc on a 5-ft G.E. SF-96 silicon on Chromosorb column at 96°.

Anal. Calcd for $C_3H_3N_2F$: C, 54.55; H, 2.75; N, 25.45. C, 54.9; H, 2.88; N, 26.05.

The F^{19} spectrum of the sample had peaks, each a quartet, $J_{HF} = 4$ cps, at $\phi +102.7$ and $+105.4$. The proton nmr spectrum exhibited two methyl peaks, each as doublet ($J_{HF} = 4$ cps) at δ 2.11 and 2.20. Observing the proton spectrum while irradiating F^{19} at 23,836 cps LSB collapsed one methyl doublet to a singlet; at 23,936 cps LSB, crystal frequency 37.617 Mc, the other methyl doublet became a singlet.

Registry No.—II, 10036-38-1; IV, 10039-65-3; i, 10036-39-2; V, 10036-40-5; *cis* VI, 10036-41-6; *trans* VI, 10036-42-7; XII, 10036-43-8; XI, 10036-44-9; *cis*-1,2-dicyano-1-fluoro-1-propene, 367-07-7; *trans*-1,2-dicyano-1-fluoro-1-propene, 367-08-8; tetrafluorohydrazine, 10036-47-2.

Direction of Cleavage of Primary Ozonides in the Methanolic Ozonolyses of Styrene, Propenylbenzene, and 2-Methylpropenylbenzene

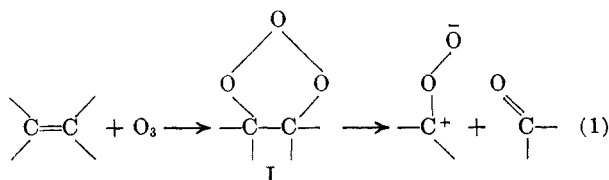
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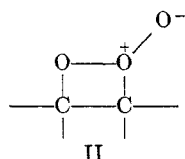
The carbonyl component/methoxyhydroperoxide ratios resulting from ozonolysis of the title olefins in methanol have been determined at -65 to -70° . A rationale for these observations has been offered in terms of the direction of cleavage of the primary ozonides. Some properties of the hydroperoxidic products are discussed.

It has proved possible to rationalize many of the facts associated with the ozonolysis of olefins on the basis that a "primary ozonide" I¹ is first formed, and that this undergoes heterolysis according to a proposal by Criegee,⁸ as shown in eq 1. With a primary ozonide



such as III, derived from an unsymmetrical olefin, alternate modes of cleavage are possible (eq 2).

(1) Structure I presently enjoys rather universal acceptance as most accurately representing the initial ozone-olefin addition compound,²⁻⁵ the "molozonide" II^{6,7} having been generally superseded.



(2) P. S. Bailey, S. B. Mainthia, and C. J. Abshire, *J. Am. Chem. Soc.*, **82**, 6136 (1960).

(3) R. Huisgen, *Angew. Chem. Intl. Ed. Engl.*, **2**, 565 (1963).

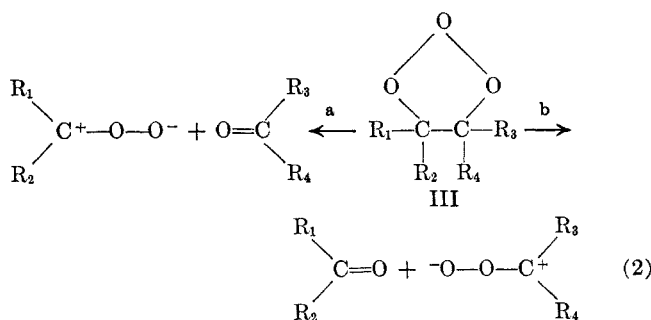
(4) (a) F. L. Greenwood, *J. Org. Chem.*, **29**, 1321 (1964); (b) F. L. Greenwood and B. J. Haske, *Tetrahedron Letters*, 631 (1965).

(5) P. S. Bailey, J. A. Thompson, and B. A. Shoulders, *J. Am. Chem. Soc.*, **88**, 4098 (1966).

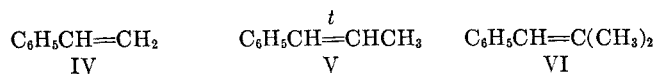
(6) H. Staudinger, *Ber.*, **58**, 1088 (1925).

(7) P. S. Bailey and S. S. Bath, *J. Am. Chem. Soc.*, **79**, 3120 (1957).

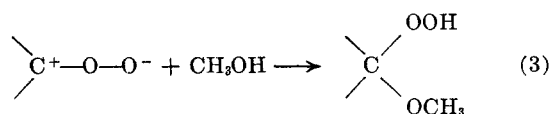
(8) R. Criegee, *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)*, **18**, 111 (1957).



The present study has dealt with the ozonolysis of unsymmetrical olefins, with a view toward gaining an insight into the factors which determine the relative importance of cleavage paths a and b. The compounds which have been ozonized at *ca.* -70° are styrene (IV), *trans*-propenylbenzene (V), and 2-methylpropenylbenzene (VI). The "participating" sol-



vent methanol was employed in order to intercept the zwitterions and convert them to isolable α -methoxyhydroperoxides (eq 3).



The products expected from these reactions are outlined in Scheme I. All these were indeed obtained,