Further elution with 20% ether–benzene (100 ml) gave in Fraction 17, methyl 7α-18-dimethoxydehydroabietate (**8**) (47 mg) as a white solid, mp 129–133°. This, on recrystallization from ether, gave the analytical sample: mp 141–143°; λ^{Nujol} 5.83, 6.68, 8.05, and 9.35 μ, no λ_{max}; nmr (cps) 429 (s, 3 H, aromatic protons), 258 (t, J = 3 cps, 1 H, C_7-β-proton), 223 (s, 3 H, C_{15}-OCH_3), 206 (s, 3 H, C_7-α-OCH_3), 185 (s, 3H, C_{18}-OCH_3), 91 (s, 6 H, C_{19}- and C_{20}-protons), 79 (s, 3 H, C_{16}-protons), 71 (s, 3 H, C_{17}-protons).

Anal. Calcd for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15. Found: C, 73.65; H, 9.05.

13-Isopropyl-podocarpa-6,8,11,13-tetraen-15-oic Acid Methyl Ester (Methyl Δ^6-Dehydrodehydroabietate) (7).—The mother liquor from the recrystallization of **3** above was evaporated to dryness and the residual oil (745 mg), composed of methyl Δ^6-dehydrodehydroabietate (**7**), methyl 7β-methoxydehydroabietate (**5**), methyl 7α-methoxydehydroabietate (**3**), and methyl 18-methoxydehydroabietate (**4**) (identified **3**, **4**, and **5** by their known relative retention times) was chromatographed over alumina (25 g).

Elution with 30% benzene–hexane mixture (200 ml) (Fraction 9, 10) and 40% benzene–hexane mixture (100 ml) (Fraction 11) gave methyl Δ^6-dehydrodehydroabietate[19] (**7**) as oil (120 mg) with 80% purity. Impurities are **3** and **5**. Further elution with 40% benzene–hexane mixture (50 ml) (Fraction 12) gave pure **7** (26 mg): λ_{max}^{EtOH} 265 and 220 mμ; λ^{neat} 3.37 (aromatic), 5.80 (>C=O), 6.25 (>C=C<), 6.42, 6.73 (aromatic), 8.06 (C–O ester), 9.27, 12.18 (aromatic), and 14.57 (*cis*-CH=CH) μ; nmr (cps) 428 (m, 34, aromatic protons), 394 (a pair of doublets, J_{AB} = 9 cps, J_{AX} = 3 cps, 1 H, C_7-proton), 346 (a pair of doublets, J_{AB} = 9 cps, J_{AX} = 2.5 cps, 1 H, C_6-proton), 220 (s, 3 H, C_{15}-OCH_3), 177 (t, J = 3 cps, C_5-proton), 166 (m, J = 7 cps, C_{18}-proton), 85 (s, 3 H, C_{16}-protons), 75 (d, J = 7 cps, C_{19}- and C_{20}-protons), 65 (s, 3 H, C_{17}-protons).

The identity was further confirmed by the relative retention time in 15% DEGS column (6 × 3/16 in.) at 230° with the known data (methyl stearate[20] as internal standard).

Further elution with benzene (100 ml) (Fraction 21) and 10% ether–benzene (200 ml) (Fraction 22, 23) gave solid **3** (131 mg) mixed with **5**.

Registry No.—**1**, 127-25-3; NBS, 128-08-5; **2a**, 25236-84-4; **3**, 25236-85-5; **4**, 25236-86-6; **7**, 18492-76-7; **8**, 25236-88-8.

Acknowledgment.—We wish to thank Mr. G. Bourdreaux of Southern Utilization Research and Development Division, New Orleans, Louisiana, for taking the nmr spectra.

(20) F. H. Max Nestler and D. F. Zinkel, *Anal. Chem.*, **39**, 1118 (1967).

Synthesis of N,N,N′-Trifluoroamidines[1]

DONALD L. ROSS, CLIFFORD L. COON, AND MARION E. HILL

Organic and Polymer Chemistry Division, Stanford Research Institute, Menlo Park, California 94025

Received January 26, 1970

The dehydrofluorination of 1,1-bis(difluoramino)alkanes yielded the corresponding N,N,N′-trifluoroalkylamidines in good yield. The geometric isomers of these compounds were separated, and conformations are proposed. The direct fluorination of fluoroalkylamidines in the solid phase produced only one isomer of the corresponding N,N,N′-trifluoroamidines, $R_fC(=NF)NF_2$. The addition of methanol to the fluorimino group followed by fluorination gave $R_fC(NF_2)_2OCH_3$.

The fluorination of nitrogen bases with elemental fluorine has received considerable attention during recent years.[2] The solution fluorination of amines[3] and N-alkylcarbamates or -ureas[4] have yielded the corresponding alkyl difluoramines, and the fluorination of nitro aromatic amines produced nitro aromatic difluoramines.[5]

The synthesis of N-haloamidines to give N-chloro-, -bromo-, and -iodoamidines has been studied extensively.[6–9] The synthesis of the first N-fluoroamidine, tetrafluoroformamidine, has been reported[10] as well as some reactions involving this compound.[2,11] Our interest in other N,N,N′-trifluoroamidines prompted us to investigate methods of preparing these compounds by two methods: (a) the dehydrofluorination of terminal geminate difluoramino compounds, and (b) the direct fluorination of amidines.

Terminal geminate difluoraminoalkanes are readily prepared by the reaction of difluoramine with aldehydes.[12] The dehydrofluorination of these compounds with base occurs rapidly to give moderate to high yields of N,N,N′-trifluoroamidines. The kinetics of the base-catalyzed dehydrofluorination of several difluoraminoalkanes has been studied previously,[13,14] but dehydrofluorination has not been applied to the synthesis of trifluoroamidines on a laboratory scale. Solution fluorination was not a practical method for the synthesis of trifluoroamidines, although trace amounts of N-fluoramino compounds were detected in the solution fluorination of acetamidine, butyramidine, and heptafluorobutyramidine.[9] The solid phase fluorination of electronegatively substituted amidines yielded the desired trifluoroamidines whereas considerable decomposition and C-fluorination resulted when unsubstituted alkyl amidines were fluorinated.

Results and Discussion

In this study the compounds prepared by dehydrofluorination were N,N,N′-trifluoropropionamidine (**1**), N,N,N′-trifluorohexanamidine (**2**), and 2-chloro-N,N,-N′-trifluoropropionamidine (**3**). The *syn* and *anti* iso-

(1) This work was supported by the Naval Ordnance Systems Command, Contract No. N00017-68-C-4414, and by the Advanced Research Projects Agency monitored by the Bureau of Naval Weapons, Contract No. NOw-64-0207-d.

(2) J. K. Ruff, *Chem. Rev.*, **67**, 665 (1967).

(3) C. M. Sharts, *J. Org. Chem.*, **33**, 1008 (1968).

(4) V. Grakauskas, Abstracts, 3rd International Symposium on Fluorine Chemistry, Munich, Germany, Sept 1965, p 220.

(5) C. L. Coon, M. E. Hill, and D. L. Ross, *J. Org. Chem.*, **33**, 1387 (1968).

(6) P. Robin, *C. R. Acad. Sci.*, **177**, 1304 (1923).

(7) J. Goerdeler and K. Wember, *Chem. Ber.*, **86**, 400 (1953).

(8) H. C. Stevens and O. Grummitt, *J. Amer. Chem. Soc.*, **74**, 4876 (1952).

(9) C. L. Coon, D. L. Ross, and M. E. Hill, *Tetrahedron Lett.*, **30**, 3537 (1966).

(10) R. J. Koshar, D. R. Husted, and C. D. Wright, *J. Org. Chem.*, **32**, 3859 (1967).

(11) W. C. Firth, Jr., *ibid.*, **33**, 3489 (1968).

(12) K. F. Mueller and W. E. McQuistion, U. S. Patent 3,337,627 (1967).

(13) S. K. Brauman and M. E. Hill, *J. Amer. Chem. Soc.*, **89**, 2131 (1967).

(14) S. K. Brauman and M. E. Hill, *J. Org. Chem.*, **34**, 3381 (1969).

mers of these compounds were separated and characterized. The direct fluorination of difluoronitroacetamidine hydrochloride[15] and heptafluorobutyramidine hydrochloride[16] in the solid phase produced only one isomer of the corresponding N,N,N′-trifluoroamidines, perfluorobutyramidine (**4**), and N,N,N′-trifluorodifluoronitroacetamidine (**5**). The nucleophilic addition of methanol to **4** and **5** was demonstrated, and fluorination of the adducts produced the methyl ethers, 1,1-bis(difluoramino)heptafluorobutyl methyl ether (**6**) and 1,1-bis(difluoramino)-2,2-difluoro-2-nitroethyl methyl ether (**7**).

Trifluoroamidines by Dehydrofluorination of 1,1-Bis(difluoramino)alkanes.—The synthesis of 1,1-bis(difluoramino)alkanes was readily accomplished by the reaction of the corresponding aldehydes with difluoramine in sulfuric acid solution. These bis(difluoramino)alkanes were dissolved in methylene chloride and were treated with pyridine. Optimum yields of

$$RC(NF_2)_2H + C_5H_5N \longrightarrow RC(=NF)NF_2 + C_5H_5N\cdot HF$$

1, R = CH_3CH_2–
2, R = $CH_3(CH_2)_4$–
3, R = $ClCH_2CH_2$–

trifluoroamidines were obtained when 0.33 mol equiv of pyridine was used for the preparation of **3**, and 1 mol equiv was used for **1** and **2**. No correlation could be found between the amount of pyridine required and the bis(difluoramino)alkane used. Other bases such as piperidine, quinoline, or aqueous sodium hydroxide were used, and dehydrohalogenation of other difluoramino compounds using alkali metal fluorides have been reported,[17] but in our case pyridine gave higher yields and cleaner reaction mixtures.

The trifluoroamidines **1**, **2**, and **3** were obtained as 1:1 mixtures of the *syn* and *anti* isomers.[18] After distillation it was observed that the collected fractions contained varying amounts of the isomers. Although it may be possible to separate the isomers by distillation, the separation of small amounts of mixtures was more easily accomplished by glpc. The isomer with the shorter retention time was designated A and that with the longer retention time, B.

N,N,N′-Trifluoropropionamidine (**1**) was first prepared and its isomers were separated. Nmr analysis of the isomers gave identical proton spectra with the same splitting and chemical shifts. The ^{19}F spectra differed in that the NF_2 peak (φ^* −47.0) of isomer A was downfield from the NF_2 peak (φ^* −43.7) of isomer B. Conversely, the C=NF peak (φ^* −11.3) of isomer A was upfield from the C=NF peak (φ^* −16.2) of isomer B. These same relative shifts were observed for all of the isomeric trifluoroamidines prepared in this study. On the basis of the spectral data for **1**, no structural assignment could be made with absolute certainty. However, on the basis of volatility observed in the distillations which agreed with the relative retention times on glpc, the more volatile isomer A was assigned the *anti*-NF_2,NF structure, and the less volatile isomer B was assigned the *syn*-NF_2,NF structure.

Another trifluoroamidine, N,N,N′-trifluorohexanamidine (**2**), was also prepared in the same manner as **1**. Results of the proton and fluorine nmr analyses of **2** were essentially the same as **1**; no differences were observed in the proton spectra of the two isomers of **2**. When one considers the effect of dipole moment upon the volatility of the two isomers, the more polar isomer B should be the least volatile and *vice versa*. Distillation of 1:1 isomer mixture of **2** gave fractions enriched in each isomer. Glpc analysis showed that the first fraction was rich in isomer A and the last fraction was rich in isomer B. Comparison of this data with the molecular model of each isomer further supported the structural assignments of the isomers.

While working with the trifluoroalkylamidines it was noted that the isomers were quite stable to the conditions of glpc separation or distillation. In attempts to isomerize **2**, a 2.5:1 mixture of A:B was heated neat and in methanol solution in sealed glass tubes to 60° for 15 hr. The same 2.5:1 mixture in methanol containing *p*-toluenesulfonic acid was stirred at 60° for 15 hr; in these three cases, the ratio of isomers remained unchanged. Therefore, we conclude that the energy barrier between the less stable and the more stable isomer is sufficient to prevent isomerization under these conditions. Perhaps more severe conditions would cause isomerization, but further attempts were considered too hazardous.

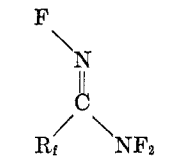
Since the nmr spectral data of **1** and **2** did not allow an assignment of isomers, a third trifluoroamidine was examined for a possible distinction of isomers. 2-Chloro-N,N,N′-trifluoropropionamidine (**3**) was prepared in the same manner as **1** and **2**, and the isomers were separated. The proton nmr spectra of the two isomers of this compound showed the same chemical shifts, and the splitting patterns of $ClCH_2$ group were identical. However, the two overlapped triplets of the CH_2C=NF group of isomer A showed a fine splitting not evident in isomer B. This result of long range H–F coupling was indicative that the structural assignment to isomer A was correct, but more supporting evidence is needed.

Trifluoroamidines by Fluorination of Amidines.—Other than tetrafluoroformamidine, pentafluoroguanidine,[10] and 1-[bis(difluoramino)fluoromethyl]-1,2,3,3-tetrafluoroguanidine,[19] the synthesis of compounds containing the trifluoroguanyl group by direct fluorination have received little attention. In order to demonstrate the feasibility of this method of synthesis, two amidines were chosen for fluorination in which the alkyl side chain would not be affected by the action of elemental fluorine. Heptafluorobutyramidine hydrochloride[16] in the solid phase was treated with fluorine diluted with nitrogen to give a liquid which was condensed from the exit gases of the reaction mixture.

(15) E. R. Bissell, *J. Org. Chem.*, **28**, 1717 (1963).
(16) W. L. Reilly and H. C. Brown, *J. Amer. Chem. Soc.*, **78**, 6032 (1956).
(17) A. L. Logothetis and G. N. Sausen, *J. Org. Chem.*, **31**, 3689 (1966).
(18) The same ratio of isomers was observed in kinetic studies when **1** was formed in 30% aqueous diglyme.[14] In this kinetic study where water acts as the base and in another study[17] in which metal fluorides were used as the base, it appeared that steric factors alone determined the stereochemistry of the final products.
(19) J. J. Hoekstra, U. S. Patent 3,361,815 (1962).

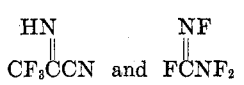
The liquid was purified and identified as perfluorobutyramidine (**4**). The major portion of the solid material remaining in the reaction was the butyramidine hydrofluoride. The use of an alkali metal fluoride as a diluent has been described.[20] By mixing the hydrochloride with sodium fluoride prior to the fluorination, less of the hydrofluoride formed and better yields of product were obtained. In contrast to the 1:1 *syn*:*anti* isomeric ratio of products observed with the hydroalkylamidines, only one isomer of **4** was obtained.[21] The ir spectrum of this compound was consistent with the assigned structure, and an nmr spectrum gave signals characteristic of the C_3F_7 group.[22,23] The NF_2 group (singlet at φ^* −42.8) was as expected, but in this instance the C=NF group occurred at φ^* −45.81.

This downfield shift is in keeping with wide variance of chemical shifts observed for the C=NF group which is strongly affected by the types of groups attached to it. For example, the C=NF group of $C_3F_7CF{=}NF$ occurs at φ^* 14.4.[23] The less sterically hindered *anti*-



4, R_f = C_3F_7–
5, R_f = O_2NCF_2–

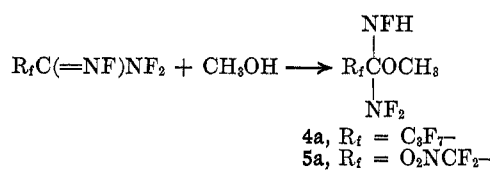
NF_2,NF structure is proposed for **4**. Other investigators[10,22] assigned the structures



to these compounds by extending the results of work on *cis* and *trans* olefin systems, and $C_3F_7CF{=}NF$ has been reported[23] but no conformation was given. Since none of these systems appeared applicable to the trifluoroamidines, the assigned configuration is preferred at this time. Other attempts to prepare **4** by the fluorination of the amidine or its hydrochloride in acetonitrile were unsuccessful. Only the hydrofluoride was obtained from these reactions due to the presence of large amounts of HF arising from the liquid-phase fluorination of acetonitrile.[24]

Difluoronitroacetamidine hydrochloride[15] was fluorinated in the same manner as heptafluorobutyramidine to give N,N,N′-trifluorodifluoronitroacetamidine (**5**). The fluorination gave a low yield mixture of five low-boiling products; nmr analysis of this mixture showed the presence of only one isomer of the desired trifluoroamidine **5**. Two of the products were separated from the mixture by glpc. One product was identified as difluoronitroacetonitrile by comparison of its ir spectrum with that of a known sample.[15] The second product was the desired trifluoroamidine **5**, whose nmr spectrum showed only one isomer with the expected singlets for the fluorimino and difluoramino groups; however, the peak at φ^* 86.1 for the O_2NCF_2 group was a quintet. Normally a 1:1:1 triplet results for the O_2NCF_2 group when no α hydrogens or fluorines are present. This type of triplet, due to coupling of fluorine (spin $^1/_2$) with nitrogen (spin 1), was shown to be characteristic of this group by obtaining the nmr spectra of $O_2NCF_2COOCH_3$, O_2NCF_2COCl, and O_2NCF_2CN.[15] Therefore, the φ^* 86.1 quintet of **5** arises from further splitting of the 1:1:1 triplet by the fluorine of either the fluorimino or the difluoramino group or both.

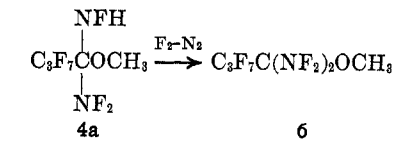
Since the cyano group of aliphatic perfluoronitriles will add ammonia, amines,[16] mercaptans,[25] and hydrogen cyanide,[22] it was of interest to determine if the trifluoroguanyl group of trifluoroamidines was sufficiently electrophilic to undergo a similar nucleophilic addition. The hydroalkyl trifluoroamidines were unreactive even in the presence of basic catalysts, but the perfluoroamidines added methanol without the aid of a catalyst.



4a, R_f = C_3F_7–
5a, R_f = O_2NCF_2–

The intermediate fluoraminodifluoraminoalkyl methyl ethers **4a** and **5a** could not be isolated from the reaction mixture without decomposition, but the presence of these compounds was shown by nmr analysis of the reaction mixtures. The ^{19}F nmr spectra of **4a** and **5a** were very characteristic, particularly the spectrum of **4a**. Since **4a** contains an asymmetric carbon, the NF_2 group occurred at φ^* −20.6 as two singlets separated by 48 Hz, and the NFH group appeared at φ^* 145.8 as two multiplets separated by 47 Hz. The pattern for the C_3F_7 group was well defined. Nmr analysis of a reaction solution containing excess methanol revealed that exchange of NF**H** with CH_3**OH** occurred to the extent that the φ^* 145.8 doublet (N**F**H) collapsed to a singlet. The proton nmr spectrum of this solution gave a singlet at τ 4.84 for N**F**H and CH_3**O**H, a singlet at τ 6.10 for $COCH_3$, and a singlet at τ 6.54 for CH_3**O**H. When no proton exchange can occur, CH_3**O**H is normally upfield from CH_3**O**H.

The presence of **4a** was further confirmed by fluorination to give the corresponding bis(difluoramino)alkyl



4a **6**

methyl ether (**6**) whose structure was confirmed by infrared, nmr, and elemental analysis.

The addition of methanol to **5** gave results similar to **4**. On the other hand, the fluorination of the methanol

(20) R. S. Koshar, D. R. Husted, and R. A. Meiklejohn, *J. Org. Chem.*, **31**, 4232 (1966).

(21) This stereospecificity was consistent with the results of others who have reported the formation of only one isomer in similar solid state fluorinations.[10] The stereospecificity in these cases is probably dependent upon the mechanism of the fluorination and may be analogous to that observed in catalytic hydrogenations in which the catalyst surface is an important factor.

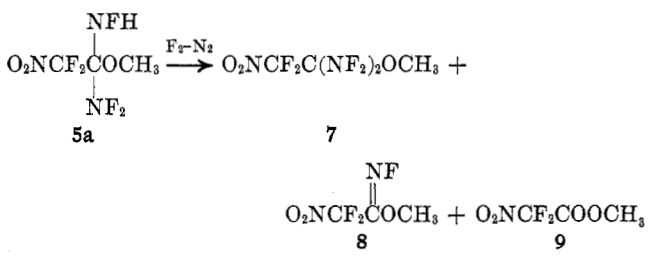
(22) W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **33**, 3625 (1968).

(23) R. A. Mitsch, *J. Amer. Chem. Soc.*, **87**, 328 (1965).

(24) S. P. Makarov, I. V. Ermakova, and V. A. Shpanskii, *Zh. Obshch. Khim.*, **36** (8), 1419 (1966); *Chem. Abstr.*, **66**, 2428 (1967).

(25) H. C. Brown and R. Pater, *J. Org. Chem.*, **27**, 2858 (1962).

adduct **5a** gave three products (**7**–**9**) in equal amounts. Each compound was separated by glpc and characterized by nmr and ir analysis. The instability of the



fluoramino intermediate **5a** is demonstrated in this reaction. The desired ether **7** was obtained in addition to the fluorimino ester **8**, which likely formed before fluorination by the loss of HNF_2. Hydrolysis of **8** by water produced in the reaction of HF with glass gave **9**, methyl difluoronitroacetate;[26] the ir and nmr spectra of **9** were superimposable on those of a known sample.

Experimental Section

Caution.—It is necessary to use protective clothing and remote handling equipment when working with NF compounds. All compounds described in this work are shock sensitive and highly explosive to varying degrees. The compounds were handled and stored in dilute solutions, and only small amounts were isolated neat for characterization. Elemental analysis of some of the compounds could not be obtained owing to repeated explosions during analysis; characterization was based on ir and nmr data.

General.—Fluorine was obtained from the General Chemical Division of the Allied Chemical Corp. and was always diluted in stream with nitrogen prior to fluorination. 1,1-Bis(difluoramino)propane was supplied by Aerojet-General Corp. in Aroclor 1248 (a high-boiling polychloropolyphenyl, Monsanto Chemical Co.); other bis(difluoroamino)alkanes were prepared from their parent aldehydes using a previously reported procedure.[12]

Elemental analyses were performed by Stanford University Microanalytical Laboratory, Stanford, Calif. Infrared spectra were run on a Perkin-Elmer 137 Infracord spectrophotometer, and nmr spectra were run on a Varian HA-100 spectrometer. Values for the ^1H chemical shifts are given in τ units with respect to tetramethylsilane as an internal reference, and values for the ^{19}F chemical shifts are given in φ^* units[27] with respect to trichlorofluoromethane as an internal reference. A Varian Aerograph 1521 gas chromatograph equipped with a thermal conductivity detector was used for all glpc analyses; large amounts of mixtures were separated using an Aerograph Autoprep A-700 gas chromatograph.

N,N,N′-Trifluoropropionamidine (1).—To a stirred solution of 0.50 g (0.0035 mol) of 1,1-bis(difluoramino)propane in 2.63 g of Aroclor at 25° was added dropwise over 2 min a solution of 0.27 g (0.0038 mol) of pyridine in 1.0 g of Aroclor. The resulting cloudy yellow mixture was stirred for 1 hr at 25°. The desired product was evaporated from the reaction mixture using a water aspirator vacuum, and the condensate was collected in a U tube cooled to −78° to give 0.39 g (90%) of **1**. The condensate contained only the *syn* and *anti* isomers as shown by glpc and nmr analysis.

Anal. Calcd for $C_3H_5F_3N_2$: C, 28.58; H, 4.00; N, 22.23. Found: C, 28.61; H, 3.91; N, 21.92.

The isomers were separated by glpc using a 20 ft × 3/8 in. column (15% Kel-F oil on 60–80 mesh Chromosorb P) at 83°. The ir (gas) spectra of the two isomers were identical: 3.31 (w), 3.35 (w), 3.42 (w), 6.80 (w) CH; 6.79 (w) CH_2; 7.25 (w) CH_3; 6.06 (w) C=N; 9.30 (w); 10.62 (w), 11.00 (s), and 11.55 μ (s) NF. Nmr: isomer A (hexachlorobutadiene), τ 8.73 (t, 3, J = 7.5 Hz, CH_3), 7.27 (two overlapped quartets, 2, J = 7.5 Hz, CH_2), φ^* −47.0 (s, 2, NF_2), −11.3 (s, 1, C=NF); isomer B, τ 8.70 (t, 3, J = 7.5 Hz, CH_3), 7.28 (two overlapped quartets, 2, J = 7.5 Hz, CH_2), φ^* −43.7 (s, 2, NF_2), −16.2 (s, 1, C=NF).

N,N,N′-Trifluorohexanamidine (2).—A stirred solution of 18 g (0.097 mol) of 1,1-bis(difluoramino)hexane in 50 ml of trichlorofluoromethane was cooled to 0–5°, and a solution of 8.2 g (0.098 mol) of pyridine in 20 ml of ether was added dropwise over 20 min. The mixture was stirred for 15 hr at ambient temperature and was then washed with 20 ml of water followed by 20 ml of dilute HCl and 20 ml of water. The organic phase was dried ($MgSO_4$) and evaporated to give 11.3 g (70% crude) of **2** as a light yellow liquid. Glpc and fluorine nmr analysis showed that the liquid contained the *syn* and *anti* isomers in a 1:1 ratio; distillation gave 10.01 g (62%) of **2** as a clear colorless liquid, bp 72° (80 mm), $n^{27}D$ 1.3841.

Anal. Calcd for $C_6H_{11}F_3N_2$: C, 42.85; H, 6.59; N, 16.67. Found: C, 43.54; H, 6.68; N, 16.28.

The isomers were separated by glpc using a 5 ft × 0.25 in. column (30% SE-30 on 80–100 mesh Chromosorb P) at 70°. The ir (neat) spectra of the isomers were identical: 3.38 (m) and 3.46 (w) CH; 6.10 (w) C=N; 6.86 (m) CH_2; 7.25 (w) CH_3; 10.1 (w), 10.7 (w), 11.1 (s), and 11.65 (s) NF; 13.7 μ (w). Nmr: isomer A ($CDCl_3$), τ 9.09 (t, 3, J = 7 Hz, CH_3), 8.63 (m, 4, J = 3 Hz, $CH_3CH_2CH_2$), 8.26 (t, 2, J = 7 Hz, CH_2CH_2C=NF), 7.31 (two overlapped triplets, 2, J = 7 Hz, CH_2C=NF), φ^* −45.5 (s, 2, NF_2), −9.3 (s, 1, C=NF); isomer B, τ 9.08 (t, 3, J = 7 Hz, CH_3), 8.62 (m, 4, J = 3 Hz, $CH_3CH_2CH_2$, 8.28 (m, 2, J = 7 Hz, CH_2CH_2C=NF), 7.38 (two overlapped triplets, 2, J = 7 Hz, CH_2C=NF), φ^* −42.4 (s, 2, NF_2), −15.7 (s, 1, C=NF).

2-Chloro-N,N,N′-trifluoropropionamidine (3).—A solution of 0.21 g (0.0026 mol) of dry pyridine in 10 ml of methylene chloride was added dropwise during 10 min to a stirred solution of 1.40 g (0.078 mol) of 1-chloro-3,3-bis(difluoramino)propane in 100 ml of methylene chloride at 5–10°. The initially colorless mixture was stirred for 15 hr at ambient temperature, the precipitate that formed was removed, and the filtrate was treated with activated charcoal and filtered. The solvent was evaporated leaving a pale yellow liquid, 0.96 g (64%) of **3**. Glpc analysis showed only two peaks, ratio 1:1, corresponding to the *syn* and *anti* isomers. The isomers were separated by glpc using a 5 ft × 0.25 in. column (15% SE-30 on 80–100 mesh Chromosorb P) at 70°. Nmr: isomer A ($CDCl_3$), τ 6.80 (two overlapped triplets, 2, J = 6 Hz, CH_2C=NF), 6.26 (t, 2, J = 7 Hz, CH_2Cl), φ^* −46.5 (s, 2, NF_2), −14.6 (s, 1, C=NF); isomer B, τ 6.89 (two overlapped triplets, 2, J = 6 Hz, CH_2C=NF), 6.25 (t, 2, J = 7 Hz, CH_2Cl), φ^* −42.8 (s, 2, NF_2), −20.9 (s, 1, C=NF).

Perfluorobutyramidine (4).—A 0.9-g sample (0.0036 mol) of dry powdered heptafluorobutyramidine hydrochloride[16] was mixed thoroughly with 0.9 g of powdered sodium fluoride. The mixture was placed in a U tube in alternating layers with glass wool. The tube was flushed with nitrogen, and a 1:3 mixture of fluorine–nitrogen was passed through the U tube at 20 ml/min for 4 hr. During the reaction the U tube became slightly warm, *ca.* 40°. The exit gases were passed first through a 0° trap and then through a −78° trap. The 0° trap contained mainly water, and the −78° trap contained 0.7 g (73% crude) of **4** as a clear colorless liquid that was 72% pure by glpc analysis. This liquid contained only one isomer of **4** which was isolated by glpc using a 20 ft × 3/8 in. column (15% Kel-F oil on 60–80 mesh Chromosorb P) at 70°. The product was a low-boiling liquid: bp 20° (229 mm); ir (gas) 6.20 (w) C=N; 7.45 (m); 8.05 (s) CF; 8.80 (m), 9.10 (w); 10.0 (w), 10.25 (w), 11.25 (s) and 11.70 (w) NF; 13.35 (s), 13.95 μ (m); nmr (CCl_4) φ^* −45.8 (s, 1, C=NF), −42.8 (s, 2, NF_2), 80.2 (t, 3, J = 9.6 Hz, CF_3), 109.6 (m, 2, J = 9.6 Hz, CF_2C=NF), 123.9 (m, 2, J = 9.6 Hz, CF_3CF_2).

1,1-Bis(difluoramino)heptafluorobutyl Methyl Ether (6). (a) **Addition of Methanol to 4.**—In a glass reactor equipped with Teflon needle valves and a magnetic stirring bar was placed 1.76 g (6.6 mmol) of **4**, 0.85 g (26.4 mmol) of methanol, and 1 g of carbon tetrachloride as solvent. The vessel was sealed, and the two-phase mixture was stirred at ambient temperature for 72 hr; after 24 hr the mixture became one phase. All attempts to isolate the methanol adduct neat were unsuccessful; the adduct was stable only in solution. Nmr analysis of the reaction mixture showed that the addition of methanol was complete after 72 hr. The product, 1-fluoramino-1-difluoraminoheptafluorobutyl methyl ether (**4a**), gave the following nmr (CCl_4–CH_3OH): φ^* −20.6 (two singlets separated by 48 Hz, NF_2), 81.5 (t, 3, J = 12 Hz, CF_3), 117.8 (m, 2, CF_2CO), 126.0 (m, 2, CF_3CF_2), 145.8 (s, 1, NFH), τ 6.10 (s, $COCH_3$), 6.54 (s, CH_3OH), 4.84 (s, NFH and OH).

(b) **Fluorination of 4a.**—**4a** was not isolated but was fluorinated *in situ*. The reactor containing **4a** in the CH_3OH–CCl_4

(26) E. R. Bissell, *J. Org. Chem.*, **26**, 5100 (1961).
(27) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

solution was cooled to −35° and was flushed with nitrogen. Fluorine–nitrogen, 1:9, was passed over the stirred mixture at 20 ml/min for 4 hr while the temperature was allowed to rise slowly to −5°. During the fluorination the mixture formed two phases; the upper phase was methanol and was discarded. The lower phase contained 1,1-bis(difluoramino)heptafluorobutyl methyl ether (6) in CCl_4. 6 was separated by preparative glpc using a 20 ft × 3/8 in. column (15% SE-30 on 60–80 mesh Chromosorb P) at 100° to give 0.54 g of pure product; bp 25° (25 mm), $n^{23}D$ 1.3088; ir (gas) 3.35 (w) CH; 6.90 (w), 7.50 (w); 8.10 (s) CF; 8.82 (m) COC; 10.25 (m), 10.45 (m), 11.18 (m) and 11.70 (m) NF_2; 12.50 μ (m); nmr (CCl_4) τ 5.95 (s, 3, CH_3), φ* −21.8 (s, 4, NF_2), 81.6 (t, 3, J = 12, CF_3), 115.5 (m, 2, CF_2CO), 125.2 (m, 2, CF_3CF_2).

Anal. Calcd for $C_5H_3F_{11}N_2O$: C, 19.00; H, 0.95; N, 8.87. Found: C, 19.48; H, 0.85; N, 8.63.

N,N,N'-Trifluorodifluoronitroacetamidine (5).—A 2.5-g sample (0.014 mol) of powdered difluoronitroacetamidine hydrochloride[15] was mixed thoroughly with 7.5 g of powdered sodium fluoride. The mixture was placed in a U tube in alternating layers with glass wool, and the tube was cooled in an ice water bath. The tube was flushed with nitrogen, and a 1:9 mixture of fluorine–nitrogen was passed through the U tube at 20 ml/min for 6 hr. The condensable exit gases were collected in a 0° trap and a −78° trap; the contents of the 0° trap was mainly water and was discarded. The −78° trap contained 1.2 g of a clear colorless liquid consisting of five compounds in almost equal amounts, but only one isomer of 5 was evident. 5 was isolated by preparative glpc using a 20 ft × 3/8 in. column (15% Kel-F oil on 60–80 mesh Chromosorb P) at 40°. One of the other five compounds was also isolated and identified as difluoronitroacetonitrile by comparison of its ir spectrum with that of a known sample:[15] bp of 5 *ca.* 20°; ir (gas) 6.18 (s), 7.45 (m), 7.62 (m), and 12.25 (m) NO_2; 8.05 (s) CF; 8.70 (m), 9.60 (w); 10.10 (s), 10.70 (s), and 11.15 μ (m) NF; nmr ($CDCl_3$) φ* −45.0 (s, 2, NF_2), −42.7 (s, 1, C=NF), 86.1 (quintet, 2, J = 10 Hz, CF_2).

1,1-Bis(difluoramino)-2,2-difluoro-2-nitroethyl Methyl Ether (7). (a) Addition of Methanol to 5.—A 0.5-g sample (2.6 mmol) of 5 dissolved in 3 ml of acetonitrile was placed in a glass reactor equipped with Teflon needle valves and a magnetic stirring bar. Methanol (0.4 g, 12.5 mmol) was added to the solution at 0°, the reactor was sealed, and the reaction mixture was allowed to stir at 0° for 4 hr. Nmr analysis of the mixture confirmed the presence of the methanol adduct, 1-fluoramino-1-difluoramino-2,2-difluoro-2-nitroethyl methyl ether (5a), and showed that reaction was essentially complete; nmr (CH_3CN–CH_3OH), φ* −19.8 (s, 2, NF_2), 92.0 (broad t, CF_2), 143.1 (d of heptets, J = 49.7 and 6.5 Hz, NFH).

(b) Fluorination of 5a.—Since 5a could not be isolated from the reaction mixture, the fluorination step was carried out *in situ*. The acetonitrile reaction mixture was cooled to −35°, the system was purged with nitrogen, and a mixture of 1:3 fluorine–nitrogen was passed over the stirred reaction mixture at 20 ml/min for 2 hr. The reaction mixture was warmed to ambient temperature, and the volatile products were collected in a −35° trap by vacuum transfer at 0.3 mm. Analysis of the condensate by glpc showed equivalent amounts of three main products in a large amount of acetonitrile. The three products were isolated by glpc using a 5 ft × 0.25 in. column (20% SE-30 on 80–100 mesh Chromosorb P) at 80°. In the order of increasing retention time, the compounds were identified by ir and nmr. 9, methyl difluoronitroacetate: nmr (CCl_4) τ 5.93 (s, 3, CH_3), φ* 93.4 (t, 2, J = 9.8 Hz, CF_2); ir (neat) 3.48 (w), 6.98 (m), 7.55 (s), 9.80 (s), and 10.75 (m) CH; 5.61 (s) C=O; 6.28 (s) and 12.50 (s) NO_2; 8.10 (m), 8.35 (s), and 8.60 (s) CF; 11.82 μ (m). The ir and nmr spectra of this compound were identical with the spectra of a sample prepared by a previously reported method.[26]

8, methyl 2,2-difluoro-2-nitrofluoriminoacetate: nmr (CCl_4) φ* 40.0 (s, 1, C=NF), 92.5 (t, 2, J = 8.5 Hz, CF_2); ir (neat) 3.48 (w), 6.90 (m), 7.35 (m), 7.50 (s), and 9.72 (s) CH; 6.05 (s) C=N; 6.28 (s) and 12.35 (s) NO_2; 8.10 (s), 8.38 (s), and 8.52 (s) CF; 9.38 (m) COC; 10.40 (m) and 11.20 μ (s) NF.

7, 1,1-bis(difluoramino)-2,2-difluoro-2-nitroethyl methyl ether: nmr (CCl_4) φ* −21.9 (s, 4, NF_2), 90.4 (quintet, 2, J = 12.1 Hz, CF_2); ir (neat) 3.38 (w), 7.91 (m), and 7.48 (m) CH; 6.25 (s) and 12.18 (s) NO_2; 8.00 (s), 8.18 (s), and 8.50 (s) CF; 9.10 (m) COC; 10.60 (s), 11.25 μ (s) NF.

Registry No.—**1** (*syn*), 21372-60-1; **1** (*anti*), 21372-59-8; **2** (*syn*), 25238-00-0; **2** (*anti*), 25238-01-1; **3** (*syn*), 25238-02-2; **3** (*anti*), 25238-03-3; **4**, 25356-05-2; **4a**, 25238-04-4; **5**, 25238-05-5; **5a**, 25238-06-6; **6**, 25238-07-7; **7**, 25238-08-8; **8**, 25238-09-9.

Acknowledgment.—The authors thank Dr. Eugene van Tamelen and Dr. Harry Mosher of Stanford University for their helpful suggestions concerning this work, Mrs. L. D. Steitzel for running the nmr spectra, and Mr. Derek Tegg for the separation of isomers.

Synthesis and Cycloaddition Reactions of Dehydrohydantoins

A. B. EVNIN, A. LAM, AND J. BLYSKAL

Union Carbide Research Institute, Tarrytown, New York 10591

Received February 27, 1970

Several $\Delta^{1,5}$-imidazoline-2,5-diones (dehydrohydantoins) have been prepared and their chemistry has been examined. They are active Diels–Alder dienophiles and also react with monoolefins (ene reaction) and nucleophiles (addition across the >C=N– bond). The reactivity of the dehydrohydantoins (I) depends markedly on the substituent in the 5 position with 5-H > 5-CO_2Me > 5-Ph. The dienophilic activity of the dehydrohydantoins appears to be intermediate between those of the corresponding α-dicarbonyl azo compounds and the α-diacyl olefins. The spectra of 5-phenyl-3-methyldehydrohydantoin (Ib), which is isolable and atmospherically stable, indicate that it is a cross-conjugated system similar to 3-phenylmaleimide.

In the course of studies of the Diels–Alder reaction,[1] we have made extensive use of α-dicarbonyl azo compounds, RCON=NCOR, as dienophiles. These azo compounds are three or four orders of magnitude more reactive than the corresponding olefins,[2] and the cyclic examples such as 4-phenyl-1,2,4-triazoline-3,5-dione[2d] are among the most active dienophiles known. The reasons for the remarkable reactivity of these α-dicarbonyl azo compounds are not known. Geometric factors and polarizability are certainly important; however, we suspect that the energetics of transforming an azo ester linkage into two C–N bonds and an unusually strong N–N bond[3] may also be highly favorable.

(1) (a) A. B. Evnin and D. R. Arnold, *J. Amer. Chem. Soc.*, **90**, 5330 (1968); (b) A. B. Evnin, R. D. Miller, and G. Evanega, *Tetrahedron Lett.*, 5863 (1968); (c) A. B. Evnin, A. Lam, J. Maher, and J. Blyskal, *ibid.*, 4497 (1969).

(2) (a) J. Sauer and B. Schröder, *Angew. Chem., Int. Ed. Engl.*, **4**, 711 (1965); (b) J. Sauer, *ibid.*, **6**, 16 (1967); (c) J. Sauer and B. Schröder, *Chem. Ber.*, **100**, 678 (1967); (d) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967).

(3) The dissociation energy of the N–N bond in N,N-diacylhydrazines is probably >50 kcal: E. Hedaya, R. L. Hinman, V. Schomaker, S. Theodoropulos, and L. M. Kyle, *J. Amer. Chem. Soc.*, **89**, 4875 (1967).