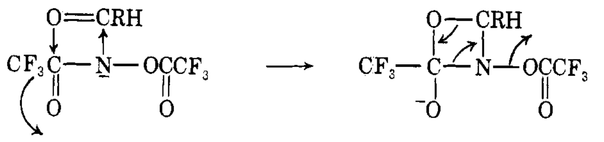
$$CF_3CONHOCOCF_3 \xrightarrow[-H^+]{\text{pyridine}} CF_3CO\bar{N}OCOCF_3 \qquad (7)$$



$$\xrightarrow[-H^+]{\text{pyridine}} RCN + 2CF_3COO^- \qquad (8)$$

The strong inductive effect of the trifluoromethyl groups is vital to this synthesis in three ways. First, the acidity of the diacylhydroxylamine is increased so that a proton can be removed from the —NH— group by pyridine. Secondly, the electrophilicity of the carbonyl group attached to nitrogen is increased sufficiently to allow participation of the carbonyl carbon in the reaction. Finally, the decreased basicity of the trifluoroacetate anion increases its effectiveness as a leaving group.

Experimental

One-gram samples of an equimolar solution of the acid and the nitrile were heated in weighed sealed glass ampoules at 150 and 200° in an oil bath whose temperature was regulated to ±0.5°. Conversion to imide was followed by two different methods, depending on the nitrile being used. With acetonitrile, the unchanged acid and nitrile were evaporated under vacuum and the ampoule reweighed. The volatile fraction was also analyzed by vapor phase chromatography on Dow Corning 550 oil-Haloport column, which separated acetic acid, acetonitrile, and acetic anhydride readily. None of the last was detected at any time. The nonvolatile imide residue was shown in infrared examination to contain no more than trace amounts of impurities except after long periods at 150° or shorter periods at 200°. The accuracy of the method was also checked by repeating one run on a larger scale, in which the conversion estimated by the small scale run was 68% and that obtained by actual distillation and isolation of products was 69%. With trifluoroacetonitrile, the reaction was conveniently followed by measuring the change in vapor pressure of the trifluoroacetonitrile in a calibrated volume before and after reaction since the boiling point of this compound was at least 130° lower than any other component. Because of its volatility, this nitrile was added to the acid by vacuum transfer during makeup of samples. Reaction times (hours) and conversions to imide (%) are given below.

Acetic Acid–Acetonitrile.—Uncatalyzed reaction at 150°: 48, 17.5; 108, 27; 156, 45; 204, 50; 318, 60. With 5% (by weight) sulfuric acid: 24, 30; 54, 45; 70.5, 52. With 5% sodium acetate: 54, 22; 132, 38.

Disproportionation of Diacetamide.—Uncatalyzed at 150°: 48, 96; 108, 90; 156, 89; 204, 87, the last two samples being partially decomposed. With 5% sulfuric acid: 54, 84; 132, badly decomposed. With 5% sodium acetate: 54, 94; 132, 90.

Trifluoroacetic Acid–Acetonitrile.—Uncatalyzed reaction at 50°: 2, 43; 6, 59; 8, 69; 24, 43 (partial decomposition). With 5% sulfuric acid: 0.92, 33; 3.2, 60. With 5% potassium trifluoroacetate: 0.92, 30; 3.2, 48.

Disproportionation of N-Acetyltrifluoroacetamide.—Uncatalyzed reaction at 150°: 2, 80.5; 6, 76; 8.2, 76; 24, 53 (partial decomposition). With 5% sulfuric acid: 1, 87; 3.3, 77 (both with some decomposition). With 5% potassium trifluoroacetate: 1, 94.

Trifluoroacetic Acid–Trifluoroacetonitrile.—Uncatalyzed reaction at 150°: 1.5, 16; 7.9. 51; 20, 84. With 5% sulfuric acid: 0.75, 77; 3, 93. With 5% potassium trifluoroacetate: 2, 79; 4.25, 91.

Disproportionation of N-Trifluoroacetyltrifluoroacetamide.—Uncatalyzed reaction at 150°: 14, 98; 30, 96. With 5% sulfuric acid: 3, 98; 5, 96.

Acetic Acid–Trifluoroacetonitrile.—Uncatalyzed reaction at 150°: 1.25, 37; 3, 64; 6, 97. With 10% sulfuric acid: 1, 73; 2, 87. With 10% sodium acetate: 1, 71; 2, 85.

Reactions at 200°.—Only approximate yields are given as decomposition was extensive. Acetic acid–acetonitrile: 24, 45; trifluoroacetic acid–acetonitrile: 8, 50; trifluoroacetic acid–trifluoroacetonitrile: 8, 50. The second of these reactions when repeated on a larger (38 g.) scale gave some $(CF_3CO)_2NH$ and $(CH_3CO)_2NH$, in addition to 18 g. (50%) of $CF_3CONHCOCH_3$.

Fluorocarbon Nitrogen Compounds. X. N,N-Difluoramines from Azoalkanes[1]

JOHN A. YOUNG AND R. D. DRESDNER

Departments of Chemistry and Chemical Engineering, University of Florida, Gainesville, Florida

Received September 24, 1962

Thermal decomposition of perfluoroazoalkanes proceeds smoothly at 350–500° and radical recombination gives chain doubling without rearrangement. Decomposition in the presence of dinitrogen tetrafluoride affords good yields of fluorocarbon N,N-difluoramines while radical addition to hexafluoropropene gives a moderate yield of perfluoroheptane. Tetrasubstituted hydrazines formed by radical addition to azoalkanes display unusual thermal stability for compounds containing a nitrogen–nitrogen bond.

Although the photochemical decomposition of fluorocarbon azoalkanes, $R_FN{=}NR_F$, has been studied rather extensively,[2-5] their thermal decomposition had received no attention prior to a very recent publication by Chambers, Tullock, and Coffman.[6] Our results, which were compiled before this paper appeared, are in entire agreement with theirs; in addition, the present work extends the synthetic use of azoalkanes to the preparation of perfluoro-N,N-difluoramines.

Either photolytic or thermal decomposition of $R_FN{=}NR_F$ leads to generation of R_F radicals. These can be coupled to give $R_F{\cdot}R_F$ or added to the parent molecule to give tetrasubstituted hydrazines; either reaction can be favored by suitable choice of reaction conditions. The isolation of isomerically pure n-C_8F_{18} from decomposition of $C_4F_9N{=}NC_4F_9$ in the present work indicates that rearrangement does not occur, and since the

---

[1] The authors are indebted to the U. S. Army Research Office and the National Science Foundation for financial support of this work. Reprint requests should be addressed to the senior author at the Denver Research Institute, Denver 10, Colo.

(2) G. O. Pritchard, H. O. Pritchard, H. I. Schiff, and A. F. Trotman-Dickinson, *Trans. Faraday Soc.*, **52**, 849 (1955).

(3) J. R. Dacey and D. M. Young, *J. Chem. Phys.*, **23**, 1302 (1955).

(4) A. P. Stefani, L. Herk, and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 2998 (1961).

(5) A. P. Stefani, L. Herk, and M. Szwarc, *ibid.*, **83**, 4732 (1961).

(6) W. J. Chambers, C. W. Tullock, and D. D. Coffman, *ibid.*, **84**, 2337 (1962).

azoalkanes are readily available by direct[7] or indirect[6,8] fluorination of nitriles, this method constitutes a useful alternative to the iodide method for doubling a fluorocarbon chain.

Decomposition in the presence of halogens or sulfur has been shown[6] to give fluorocarbon halides or polysulfides, respectively. Since dinitrogen tetrafluoride is partially dissociated even at room temperature, its reaction with $R_F\cdot$ radicals would be expected to yield R_FNF_2. Mixing equal volumes of $C_2F_5N{=}NC_2F_5$(I), N_2F_4, and nitrogen at 500° gave only NF_3, C_2F_6, and n-C_4F_{10},[9] the presence of C_2F_6 indicating that fluorination was occurring at this temperature; however, at 450° N,N-difluoropentafluoroethylamine, $C_2F_5NF_2$, was obtained in 64% conversion. The crude product contained about 15% C_4F_{10}, plus traces of CF_4, SF_6, N_2F_4, and an unsaturated compound thought to be $C_2F_5N{=}CFCF_3$. Since these impurities are easily removed by distillation or alkaline scrubbing, this method offers a much cleaner procedure for obtaining pure compounds of the type R_FNF_2 than the fluorinations before required.

N,N-Difluorotrifluoromethylamine, CF_3NF_2, was obtained by a similar reaction in 55% conversion. When $(C_4F_9)_2N_2$ was used, the yield of difluoramine fell to zero; however, the difference here is not attributable to any change in properties at C-4, as has sometimes been held, but merely reflects the higher boiling point of $(C_4F_9)_2N_2$ and the consequently greater difficulty of introducing its vapor into the reaction chamber without preliminary decomposition. Two methods were tried, saturation of a nitrogen stream by bubbling it through azoalkane held near the boiling point, and direct addition of the azo compound as a liquid, controlled by a stopcock. Neither method was successful and the products formed, $C_4F_9{\cdot}C_4F_9$ and an unsaturated compound reactive toward alkali,[10] indicated that $C_4F_9\cdot$ radicals had been formed but that mixing of the two gas streams had been ineffective.

The authors of ref. 6 observed that fluorocarbon azoalkanes initiated polymerization of various reactive olefins. With unreactive olefins such as hexafluoropropene, however, a moderate yield of the product formed by addition of two $R_F\cdot$ radicals can be obtained. Photolysis of a mixture of I and C_3F_6 gave only a 10% yield of perfluoroheptane, the major products being n-C_4F_{10} and $(C_2F_5)_2NN(C_2F_5)_2$ (II), but this figure was raised to 33% by use of an autoclave. Chromatographic analysis indicated that the product was a single isomer. Reaction of I with perfluoro-2-butyne was not successful, as at a temperature high enough for thermal decomposition of the azoalkanes the butyne underwent decomposition and trimerization to perfluorohexamethylbenzene.

Fluorocarbon isocyanates can be made[6] by thermal reaction of azoalkanes with carbon monoxide under high pressure, although the yield decreases sharply when R_F is larger than CF_3. Under photolytic conditions we were unable to effect reaction between I and CO, but did observe definite infrared evidence for C_2F_5NCO on irradiation of a mixture of I and CF_3CHO, indicating that R_FN: species may appear during photolytic as well as thermal decomposition of azoalkanes. The reaction was very complex and the probable presence of CF_3H, C_2F_5H, C_2F_6, C_3F_8, and C_4F_{10} was also indicated. The aldehyde was completely consumed but only traces of carbonyl compounds other than the isocyanate appeared.

Thermal stability of the perfluorotetraalkylhydrazines is rather surprising. Dinitrogen tetrafluoride dissociates very readily and $(CF_3CO)_4N_2$ pyrolyzes at about 325°[11]; consequently it was thought that at elevated temperatures nitrogen–nitrogen bond cleavage of the hydrazines might make bis(perfluoroalkyl)amino radicals available for cross coupling reactions. It was found, however, that even at 550° with a residence time of eleven minutes, recovery of unreacted $(CF_3)_2NN(CF_3)_2$ amounted to 84%. Decomposition products included $CF_3N{=}CF_2$, to be expected from degradation of a $(CF_3)_2N\cdot$ radical, and an unidentified material which showed infrared absorption at 4.3–4.4 μ, but which was not a low molecular weight fluorocarbon isocyanate or nitrile.

Experimental

The apparatus for thermal reactions consisted of an unpacked 1-in. nickel tube 9 in. long, the effluent gas stream from which passed through successive glass traps at −80 and −120° (heptane slush), then a third trap at −120°. Liquid nitrogen was not used because of possible explosion hazards at transition temperatures of fluoramines. A tee between the second and third traps carried a slight flow of dry nitrogen at all times to prevent diffusion of air and moisture into the product traps, which were so arranged that either could be exhausted into the vacuum system through a common duct. Inlet lines were designed so that azoalkane and N_2F_4 could be metered directly into the reactor or carried in on a metered stream of dry nitrogen, while a heated bubbler located on a bypass could be used to saturate a nitrogen stream with azoalkanes boiling above room temperature. The two reactant streams did not mix until each had entered the heated zone, as explosions had sometimes occurred in earlier work with NF_3 and C_3F_6 when these were mixed cold and heated.[12] Flow rates of reactants and any added nitrogen were measured by flowmeters, but net quantities of reactants were more accurately obtained by loss in weight of the small detachable containers, since control over the flow rates involved was not sufficiently precise for this purpose.

Except for the bubbler, the system leading to the reactor was constructed of copper tubing. For those sections which might be exposed to N_2F_4, Monel or stainless steel valves with Teflon packing and flowmeters with nickel-plated end fittings and Viton A O-rings were used; fittings on the other lines were of more prosaic and less expensive materials. Where flexibility was necessary, Tygon tubing was adequate.

In practice, the entire apparatus was continuously evacuated while the reactor was warming to temperature. The vacuum was then broken with dry nitrogen and the proper flow rates set on the respective flowmeters. After a period of time had elapsed equivalent to passage of the desired amounts of reactants (determined rather roughly by previous calibration of the flowmeters) the reactant streams were cut off and an equal flow of dry nitrogen substituted until all the reactants and products had been flushed out of the system. This procedure, which was used in order not to alter the residence times of the reactants, probably introduced a slight dilution effect, but since the tubing and reactor cross sections were not large and the flow was not rapid, such an effect should have been inconsiderable.

The reaction products were analyzed by infrared and chromatographic methods, using the following infrared bands for identi-

---

(7) J. H. Attaway, R. H. Groth, and L. A. Bigelow, *J. Am. Chem. Soc.*, **81**, 3599 (1959).

(8) J. A. Young, W. S. Durrell, and R. D. Dresdner, *ibid.*, **82**, 4553 (1960).

(9) CF_4 and SF_6 were also observed but were present initially as impurities in the N_2F_4.

(10) Probably $C_4F_9N{=}CFC_3F_7$, formed by pyrolysis of $(C_4F_9)_2N{-}N(C_4F_9)_2$.

(11) J. A. Young, W. S. Durrell, and R. D. Dresdner, *J. Am. Chem. Soc.*, **84**, 2105 (1962).

(12) R. D. Dresdner, F. N. Tlumac, and J. A. Young, *ibid.*, **82**, 5831 (1960).

fication: CF_4, 7.8; C_2F_6, 9.0, 14.0; C_4F_{10}, 7.7, 8.7, 11.1; NF_3, 11.0; $C_2F_5N = NC_2F_5$, 7.4–7.5, 8.5, 9.3; $(C_2F_5)_4N_2$, 9.1, 9.3, 11.1, 11.5; $C_2F_5NF_2$, 7.3, 8.4, 10.3, 10.6; CF_3NF_2, 7.8, 9.8, 10.5 μ. The chromatographic column was 12 m. in length, hexadecane on Celite, and was capable of giving good resolution of fluorocarbon structural isomers such as *n*- and isoperfluorohexane.

The dinitrogen tetrafluoride (of Air Products and Chemicals, Inc., manufacture) was purchased from Peninsular ChemResearch and contained small amounts of CF_4 and SF_6. Hexafluoroazomethane was made by reaction of ICN with IF_5,[3] and BrCN with AgF_2 at 100°. Neither of these gave good yields, the best (39%) being obtained from IF_5 and ICN in an autoclave at 150°. Higher azoalkanes were made as previously described.[8]

Photochemical reactions were carried out in a 15-l. bulb with an internal Hanovia 654A 200-w. water-jacketed lamp unless otherwise noted.

Pyrolysis of I.—Over a period of 1 hr., 3.3 g. of I and an equal flow of nitrogen were passed through the furnace at 500°, with an estimated residence time of about 3.2 min. Nothing condensed in the heptane slush trap. The Dry Ice condensate showed no infrared bands due to I or II, but gave all the correct bands for *n*-C_4F_{10}. Slight absorption at 5.5–5.6 μ indicated very small amounts of an impurity containing carbon–nitrogen unsaturation.

Photolysis of I.—Seventeen grams of I was irradiated for 24 hr. at room temperature, the pressure rising from 86 to 141 mm. After cooling in liquid nitrogen and removal of nitrogen formed by reaction, the condensate on vacuum transfer gave 10.5 g. of *n*-C_4F_{10} (69%) and 2.0 g. (12%) of II. The latter distilled completely at 118° and had $n^{29}D$ of 1.2833.

Reaction of I with N_2F_4.—Reaction of the azoalkane with N_2F_4 was first carried out at 500°. Using a volume ratio of 1 N_2:1 N_2F_4:1 $(C_2F_5N)_2$ and an estimated residence time of 2.4 min., no fluorocarbon N—F compounds were obtained. From the variety of colors observed in handling the very small amount of −120° condensate, it was assumed that a trace of unchanged N_2F_4 was present; however, this fraction consisted mainly of CF_4, NF_3, and C_2F_6. The first of these constituted an impurity in the N_2F_4 used; the others indicated that the N_2F_4 was acting only as a fluorinating agent. Since the material balance was poor, the nickel reactor was probably attacked also. No infrared evidence of lower nitrogen fluorides appeared. The Dry Ice condensate contained only C_4F_{10} and a little C_2F_6. From 1.1 g. of I admitted over 0.5 hr., an estimated 0.1 g. of C_4F_{10} and 0.7 g. of C_2F_6 were produced.

At 450° and using a volume ratio of $2N_2F_4$:$1(C_2F_5N)_2$, with no nitrogen, 1.1 g. of I admitted over 30 min. gave 0.3 g. of condensate at −120° and 1.0 g. at −80°. The colder trap contained a trace of CF_4 and SF_6; aside from these it was almost pure $C_2F_5NF_2$. The Dry Ice condensate, by infrared and chromatographic estimation, was composed of about 75% $C_2F_5NF_2$ and 20% C_4F_{10}, part of the latter being originally present as an impurity in the I. A weak band in the infrared at 5.5 μ can probably be ascribed to a small amount of $C_2F_5N = CFCF_3$; however, C_2F_6 was definitely absent. From the quantities given, the over-all yield of $C_2F_5NF_2$, based on I, was estimated to be 64%.

Reaction of $CF_3N = NCF_3$ with N_2F_4.—Over a period of 30 min. 1.2 g. of $CF_3N = NCF_3$ and 0.8 g. of N_2F_4 were admitted to the furnace at 450–452°. After the system had been flushed with nitrogen, the −120° trap contained 1.3 g. of condensate, the −80° trap only traces. An infrared spectrum of the crude product showed it to be mainly CF_3NF_2, plus some C_2F_6 and SiF_4, the latter apparently due to inadvertent admission of air during the nitrogen sweep. Chromatographic analysis indicated 65% CF_3NF_2, 12% SiF_4, 9% N_2F_4, 9% C_2F_4, and 5% CF_4. Based on 1.2 g. of $CF_3N = NCF_3$, these figures represent a 55% yield of CF_3NF_2.

Reaction of I with C_3F_6.—Twenty-four grams (0.09 mole) of I and 18 g. (0.12 mole) of C_3F_6 were transferred into a 5-l. Pyrex bulb and illuminated with an external Hanovia lamp. After 17 days the contents were frozen in liquid air and nitrogen pumped off. Fractionation of the condensate gave 10.0 g. recovered C_3F_6, mol. wt. 148–151, about 2 g. of unchanged azoalkane, and 3.5 g. of C_7F_{16}. Seven grams of II was also obtained in the reaction. The yield of C_7F_{16}, based on unrecovered I, was 11%. A similar reaction with a large excess (4:1 mole ratio) of C_3F_6 also gave a yield of about 10%.

The perfluoroheptane showed no infrared evidence of unsaturation and was indicated to be > 99.5% pure by chromatography. Although its structure was not ascertained, it had a slightly lower boiling point and a slightly higher refractive index than *n*-C_7F_{16}, as would be expected of a branched isomer.

Nine grams (0.034 mole) of I and 22 g. of C_3F_6 (0.146 mole) rocked at 350° in an autoclave for 18 hr. and the contents fractionated gave, exclusive of intercuts, 10.5 g. of recovered C_3F_6, 2.0 g. of recovered I, 2.2 g. of C_3F_6 dimer (perfluorodimethylcyclobutanes), 3.5 g. of C_7F_{16}, and 3.0 g. of II, plus high boiling material. By this method the yield of perfluoroheptane was 33%. The use of flow conditions for the same reaction was not investigated, but should give equal or superior conversion.

Pyrolysis of $(CF_3)_2NN(CF_3)_2$.—Six grams of $(CF_3)_2NN(CF_3)_2$ was put through the reactor at 550° over a period of 5 hr. Fractionation of the Dry Ice condensate, 6.0 g., gave 1.0 g. of material with b.p. −28 to −20°, the remainder being unchanged starting material. The volatile fraction gave the proper infrared bands for $CF_3N{=}CF_2$, but extraneous absorption and the presence of two peaks in a chromatogram indicated impurities.

Photolysis of I with CF_3CHO.—Seventeen and one half grams (0.066 mole) of I and 5.5 g. (0.058 mole) of CF_3CHO were irradiated for 4 days. Fractionation of the reaction product gave no flats between −80 and +55°. Infrared examination of rough cuts allowed identification of constituents as follows: overhead (−80°) (CF_3H, CF_4, SiF_4, C_2F_6; −30 to −5°, C_3F_8, *n*-C_4F_{10}, C_2F_5NCO; 0–25°, same as preceding plus weak bands at 2.8 and 5.6 μ. Chromatograms showed presence of four to six components in the less volatile fractions, none being predominant.

Acknowledgment.—The authors are grateful to the personnel of Peninsular ChemResearch for several helpful suggestions regarding equipment and for a comparison infrared spectrum of CF_3NF_2.