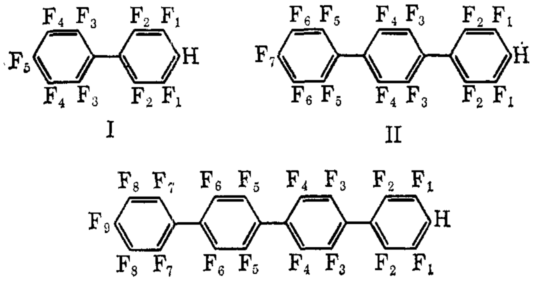
was added over 1.75 hr at 0°. After the addition was complete, the reaction mixture was slowly allowed to come to room temperature. The precipitate which consisted of the product tetra-(pentafluorophenyl)silane (69% yield) and inorganic salts was filtered. The filtrate was hydrolyzed with dilute hydrochloric acid and extracted three times with diethyl ether. The diethyl ether extracts were dried and distilled to leave 25 g of a solid which consisted of the side products of the reaction. The material was dissolved in petroleum ether (bp 60-90°) and separated by passing through an alumina (Woelm, neutral grade) column. Petroleum ether (bp 60-90°) was used as the eluent. Compounds I-III (Chart I) were recrystallized from petroleum ether (bp 30-90°).

CHART I



I II III

The F^{19} spectra were recorded on a Varian Associates V-4300B spectrometer at 40 Mc/sec with trifluoroacetic acid as an external standard (see Table II).

TABLE II

Compd	F atom	Ppm[a]	Multiplicity[b]	Integrated peak area
I	$F_1F_2F_3$	+60.3	m	6
	F_4	+83.6	m	2
	F_5	+72.9	t ($J_{F_4F_5}$ = ~20 cps)	1
II	$F_1F_2F_3F_4F_5$	+62.3	m	10
	F_6	+86.4	m	2
	F_7	+75.5	t ($J_{F_6F_7}$ = ~20 cps)	1
III	$F_1F_2F_3F_4F_5F_6F_7$	+62.8	m	c
	F_8	+83.2	m	...
	F_9	+74.0	t ($J_{F_8F_9}$ = ~20 cps)	...

[a] Trifluoroacetic acid as external standard. [b] m = multiplet; t = triplet. [c] Concentration was too low to obtain a good integration.

The H^1 spectra were recorded on a Varian A60 spectrometer. The spectra of I and II exhibited a first-order triplet of triplets centered at 7.6 ± 0.1 ppm with characteristic *o*- and *m*-fluorine-hydrogen coupling constants[4,5] ($J_{F_1H} = 10.1 \pm 0.1$ cps, $J_{F_2H} = 7.8 \pm 0.1$ cps). This observed pattern confirms the *para* orientation of the protons. Tetramethylsilane was used as the internal standard for I. The spectrum of II was obtained by using a dimethylacetamide solution (20% by weight) at 100°. The protons of the $CH_3\overset{|}{C}{=}O$ of the solvent were used as a reference point.

Acknowledgments.—The authors wish to thank J. V. Pustinger, Jr., and J. Strobel, Monsanto Research Corporation, and R. De Pasquale, Air Force Materials Laboratory, for the determination and interpretation of the nmr spectra reported in this work.

---

[4] H. S. Gutowsky, C. H. Holm, A. Saika, and G. A. Williams, *J. Am. Chem. Soc.*, **79**, 4596 (1957).

[5] J. Burdon, W. B. Hollyhead, and J. C. Tatlow, *J. Chem. Soc.*, 6336 (1965).

Organic Fluoronitrogens.[1a] V. Bis(difluoramino)difluoromethane

ROBERT J. KOSHAR, DONALD R. HUSTED,[1b] AND RUDD A. MEIKLEJOHN

Contribution No. 388 from the Central Research Laboratories, Minnesota Mining and Manufacturing Company, Saint Paul, Minnesota 55119

Received July 15, 1966

The synthesis of bis(difluoramino)difluoromethane, $F_2NCF_2NF_2$, by the direct fluorination of cyanuric chloride was recently reported.[2] The identification of the compound was based primarily on molecular weight, elemental analyses, and infrared spectral analysis.[3] During our investigations of direct fluorination, bis(difluoramino)difluoromethane was prepared by the fluorination of aminoiminomethanesulfinic acid. We wish to report the details of this synthesis as well as the properties of bis(difluoramino)difluoromethane which unequivocally establish its structure.

The direct fluorination of a mixture of aminoiminomethanesulfinic acid and sodium fluoride was carried out under mild conditions at 0° with 10% by volume of fluorine in nitrogen. In addition to the formation of a large amount of sulfuryl fluoride, the fluorination yielded bis(difluoramino)difluoromethane, difluoramidosulfuryl fluoride[4] (F_2NSO_2F), thionyl fluoride, difluoraminoperfluoromethane, nitrogen trifluoride, and other cleavage products.

Bis(difluoramino)difluoromethane is apparently formed from aminoiminomethanesulfinic acid by the replacement of hydrogen, addition to the imino bond, and carbon-sulfur cleavage. The formation of difluoramidosulfuryl fluoride is presumed to occur by the combination of difluoramino and sulfuryl fluoride radicals.

$$H_2N\overset{\overset{NH}{\|}}{C}SO_2H + 6F_2 \longrightarrow F_2NCF_2NF_2 + SO_2F_2 + 4HF$$

Bis(difluoramino)difluoromethane (8-10% yield) was isolated by gas chromatography and identified by infrared, nuclear magnetic resonance, and mass spectroscopy as well as molecular weight and elemental analyses. Difluoramidosulfuryl fluoride was identified by comparison of its infrared spectrum with the published spectrum.[4]

The vapor pressure of bis(difluoramino)difluoromethane, measured from −123 to −46°, can be expressed by the Clausius-Clapeyron equation. The

$$\log P_{\text{mm}} = 7.653 - \frac{1149}{T}$$

boiling point, obtained by extrapolation of the vapor pressure curve, is −32 ± 1°. The compound has a

---

[1] (a) Preceding paper in this series: R. [illegible] Mitsch, E. W. Neuvar, R. J. Koshar, and D. H. Dybvig, *J. Heterocyclic Chem.*, **2**, 371 (1965). (b) Deceased, Aug 5, 1965.

[2] M. A. Englin, S. P. Makarov, S. S. Dubov, and A. Ya. Yakubovich, *Zh. Obshch. Khim.*, **35**, 1416 (1965).

[3] The disclosures relating to the infrared spectrum were insufficient to enable a comparison with the spectrum of bis(difluoramino)difluoromethane obtained by the method described in this present communication.

[4] M. Lustig, C. L. Bumgardner, F. A. Johnson, and J. K. Ruff, *Inorg. Chem.*, **3**, 1165 (1964).

melting point of −162 to −159° and a liquid density of 1.50 ± 0.02 g/cc at 25°. The heat of vaporization is estimated at 5.3 kcal/mole and the Trouton's constant is 21.8.

The infrared spectrum of bis(difluoramino)difluoromethane exhibits prominent absorptions at 7.75 (s) and 7.92 μ (m) in the region for CF stretching as well as absorptions at 10.35 (vs) and 10.95 μ (s) which are attributed to NF stretching. Three unassigned absorption bands occur at 8.70 (w), 9.67 (w), and 13.02 μ (w).

The fluorine nuclear magnetic resonance spectrum, using trichlorofluoromethane as the internal reference, consists of a broad resonance absorption at ϕ^* −19.0 assigned to the NF_2 groups, and a sharp absorption at ϕ^* +112.9, assigned to the CF_2 group. The measured NF_2 to CF_2 area ratio was approximately 2:1. The mass spectrum of bis(difluoramino)difluoromethane, which also supports its structure, is given in Table I. The highest prominent mass of 102 is attributed to the cation, $F_2NCF_2^+$.

TABLE I

FRAGMENTATION PATTERN OF $F_2NCF_2NF_2$[a]

m/e	Ion	Pattern, %
14	N^+	5.3
19	F^+	3.1
26	CN^+	2.2
28	N_2^+	1.6
31	CF^+	20.8
33	NF^+	13.9
45	CNF^+	6.9
50	CF_2^+	24.4
52	NF_2^+	39.1
64	CNF_2^+	13.8
69	CF_3^+	100.0
70	Isotope	1.2
83	CNF_3^+	70.0
84	Isotope	1.0
102	CNF_4^+	16.5

[a] Sensitivity m/e 69, 59.0 divisions/μ. n-Butane sensitivity m/e 43, 125.0 divisions/μ. Only peaks greater than 1.0% are given.

Differential thermal analysis of bis(difluoramino)difluoromethane, carried out in a sealed borosilicate glass tube, indicated a slow exotherm at 335°. No evidence of decomposition was noted at the critical temperature of about 89.0°.[5]

Bis(difluoramino)difluoromethane is colorless in the gas or liquid phases and does not appear to be affected by mercury, water, or dilute aqueous alkali (*e.g.*, 10% sodium hydroxide solution) at room temperature. The compound is stored conveniently in the vapor phase at room temperature in closed borosilicate glass containers. Because of the explosive nature of N-halogen compounds in general, bis(difluoramino)difluoromethane should be handled with caution.

Experimental Section

Materials.—Aminoiminomethanesulfinic acid was obtained from the Eastman Kodak Co. The sulfinic acid was thoroughly the desiredmixed with amount of powdered sodium fluoride and the mixture was stored in a desiccator. Chromosorb P (30–60 mesh) used for the chromatographic columns was obtained from Johns-Manville and the FC-43 from the Minnesota Mining and Manufacturing Co. Fluorine was supplied by the General Chemical Division of the Allied Chemical Corp.

Methods of Analyses.—The infrared spectra were recorded by means of a Perkin-Elmer double-beam spectrophotometer (Model 21) using 2.5-cm gas cells equipped with sodium chloride windows.

The fluorine nuclear magnetic resonance shielding values (ϕ^*) were obtained with trichlorofluoromethane as the internal reference using dilutions of 20–30% by volume, according to methods previously described.[6] A Varian V-4300-2 instrument operating at 40.0 Mc was used. Perfluoroacetic acid is ϕ^* 76.5 on the above scale.

A Consolidated Electrodynamics Corp. mass spectrometer (Model 21-103C) was employed to record the mass spectrum. The ionization potential was 70 v and the ionization chamber was 250°.

Gas chromatographic analyses and isolation of products were carried out with a Perkin-Elmer vapor fractometer, Model 154-D, equipped with a thermistor detector and modified gas sampling and backflush valves. Gas samples of about 2 mmoles were usually condensed *in vacuo* in a barricaded 25-ml stainless steel coil and then allowed to warm to room temperature prior to injection into the column.

Safety Precautions.—Since explosions have occurred during the course of this research, especially during phase transitions, the synthesis, isolation, and storage of bis(difluoramino)difluoromethane even on a microscale should be carried out using suitable protective equipment.[7]

Fluorination of Aminoiminomethanesulfinic Acid.—A dry mixture of 0.75 g (6.9 mmoles) of aminoiminomethanesulfinic acid and 3.75 g of powdered sodium fluoride was placed in a 650-ml capacity rectangular brass reactor fitted at the bottom with a 2 × 10 in. monel sintered plate. The reactor was also equipped with a gas inlet located below the sintered plate and a gas outlet at the top. The outlet was connected to a borosilicate glass trap which was cooled with liquid oxygen and opened to a nitrogen atmosphere.

The reactor was cooled to an inside temperature of 0°, measured at the sintered plate, and the system was flushed with nitrogen to expel air. A gas mixture of 10% by volume of fluorine in nitrogen was metered (Kel-F rotameter) into the reactor from a 3-l. stainless steel cylinder having an initial pressure of 100 psig. A flow rate of about 45 ml/min was used until 60 mmoles of fluorine was delivered (5.3 hr). After the completion of the introduction of fluorine, the reactor was allowed to warm to room temperature and was flushed with nitrogen for 1 hr.

The product in the collection trap was transferred *in vacuo* into borosilicate glass storage bulbs. The crude product (8 mmoles) contained bis(difluoramino)difluoromethane, difluoramidosulfuryl fluoride, thionyl fluoride, difluoraminoperfluoromethane, carbonyl fluoride, nitrogen trifluoride, silicon tetrafluoride, carbon dioxide, nitrous oxide, and a relatively large amount of sulfuryl fluoride. The components were isolated by gas–liquid partition chromatography at −20° employing a 10 ft × 0.5 in. column composed of 33% by weight of FC-43[8] on Chromosorb P. Helium, at a flow rate of about 155 ml/min, was used as the carrier gas. About 0.7 mmole of bis(difluoramino)difluoromethane and 0.05 mmole of difluoramidosulfuryl fluoride were isolated. The retention time for bis(difluoramino)difluoromethane, relative to dichlorodifluoromethane as 100 and air as 0, is 138.

The crude mixture was also separated partially by fractional distillation–condensation on a vacuum line using −78, −130, and −196° receivers. The −130° trap contained the major portion of the bis(difluoramino)difluoromethane as well as sulfuryl fluoride and other products.

Anal. Calcd for CF_6N_2: C, 7.8; N, 18.2; F, 74.0; mol wt, 154. Found: C, 8.1; N, 17.9; F, 73.1; mol wt, 155.

---

(5) The critical temperature was determined by the meniscus-disappearance method.

(6) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

(7) We have operated within a 1-g limit using poly(methyl methacrylate) shielding and wearing heavy-duty face shields, leather coats, and leather gauntlets. For quantities of greater than 1 g, remote handling is recommended. Also recommended is the use of nonflammable slush baths.

(8) FC-43 (Minnesota Mining and Manufacturing Co.) is an inert fluorocarbon liquid with a boiling range of 95% min above 170° (ASTM-D86).

Acknowledgment.—The authors acknowledge the contributions of various personnel in our laboratories. Specific acknowledgment is extended to Mr. P. B. Olson for the elemental analyses and Dr. R. L. Bohon for the physical property measurements. The work described in this communication was sponsored by the Advanced Research Projects Agency and monitored by the Bureau of Naval Weapons.

Acyloxonium Ion Intermediates. Oxygen-18 Studies

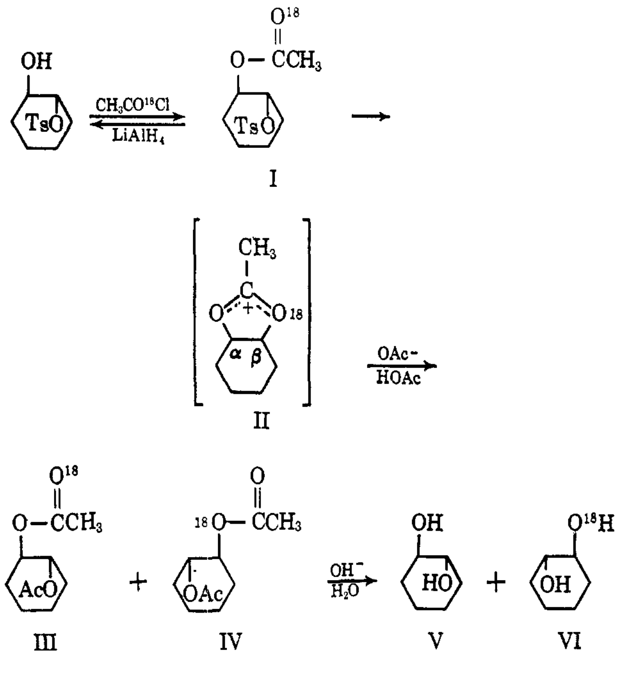
KENNETH B. GASH AND GEORGE U. YUEN

Department of Chemistry, Arizona State University, Tempe, Arizona 85281

Received December 9, 1965

The work described herein supports the "acyloxonium ion" intermediates proposed by Winstein and Buckles[1] and further demonstrates the applicability of oxygen-18-labeling experiments in following participation by neighboring groups in solvolytic reactions as described by Dolby and Schwarz.[2]

In the course of a systematic study of polyols in our laboratory, we found it very convenient to use O^{18}-labeled acetate as a means of determining the role played by "acetoxonium ion" intermediates in reactions, such as the acetolysis of 1-O-acetyl-2-O-p-toluenesulfonyl-*trans*-1,2-cyclohexanediol (I). The carboxyl-O^{18}-labeled compound I was prepared by acetylation of the mono-O-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediol with acetyl-O^{18} chloride in pyridine. Acetolysis of I with acetate ions in acetic acid gave a mixture of *trans*-diacetates-O^{18} (III + IV). Subsequent saponification of the diacetate-O^{18} (III + IV) afforded *trans*-1,2-cyclohexanediol-O^{18} (V + VI).


I II III IV V VI

Oxygen-18 analysis of the diacetate mixture (III + IV) indicated that acetolysis of I occurred with almost complete (99%) retention of O^{18}; therefore, it was apparent that loss of O^{18} *via* side reactions (*e.g.*, acetyl exchange) was not significant during this step. Most important, however, was the fact that 46% of the O^{18}, introduced into I as carboxyl-O^{18}, was found in the *trans*-1,2-cyclohexanediol-O^{18} (VI). This suggested that the "acetoxonium ion" intermediate (II) was highly symmetrical and that backside attack by an acetate ion occurred with equal ease at either the α or β carbon. For a perfectly symmetrical "acetoxonium ion" intermediate (II), a 50% incorporation of O^{18} would be expected in the final product (VI) of the reaction sequence. The experimental value of 46% approached the predicted value of 50%, if the 3% experimental error for O^{18} analysis were taken into consideration.

In the absence of potassium acetate, the acetoxonium *p*-toluenesulfonate ion pair has been known to re-form the *trans*-tosyloxyacetate (I).[3] Although in our study potassium acetate was present, which should minimize the reformation of I, it seemed important to establish clearly that the O^{18} found in *trans*-1,2-cyclohexanediol (VI) did result from the reaction sequence as outlined and not from O^{18} scrambling of the starting material (I) during the course of the reaction. From an acetolysis run of I, the starting compound was recovered from a half-completed reaction and found to contain the same O^{18} enrichment as in the original sample. Controlled hydrogenolysis of the recovered starting material (I) with lithium aluminum hydride afforded 1-O-*p*-toluenesulfonyl-*trans*-1,2-cyclohexanediol, whose O^{18} enrichment was less than 2% of that available in I. The low O^{18} enrichment suggests that there is little, if any, scrambling of the starting material during the reaction.

Although the term "acyloxonium ion" is freely used for the sake of simplicity, these results are consistent with other species, *e.g.* ion pairs, orthodiacetates, or rapidly equilibrating acetoxylcyclohexyl carbonium ions, as described by Winstein and co-workers.[3,4]

Work on other aryloxy and acyloxy arylsulfonates is in progress.

Experimental Section

Preparation of Acetic Acid-O^{18}.—Water containing 10.78% O^{18} enrichment was used. One-half gram of H_2O^{18} (0.0274 mole) was placed in a 20-ml, round-bottom flask and was frozen by immersion of the flask and content into a Dry Ice–acetone bath. After addition of a small Teflon-coated stirring bar to the flask, it was affixed with a reflux condenser, through which 2.86 g (0.0364 mole) of freshly distilled acetyl chloride was added. The reaction mixture was permitted to warm up to room temperature with constant stirring by a magnetic stirrer. As soon as evidence for reaction was noted (formation of gas bubbles), the reaction flask was cooled immediately in a Dry Ice–acetone bath. This cooling procedure was repeated as often as necessary to maintain control over the rate of reaction. After the reaction was finished, the product was refluxed for 4 hr to expel most of

---

(1) S. Winstein and R. E. Buckles, *J. Am. Chem. Soc.*, **64**, 2780 (1942).

(2) L. J. Dolby and M. J. Schwarz, *J. Org. Chem.*, **30**, 3581 (1965).

(3) R. M. Roberts, J. Corse, R. Boschan, D. Seymour, and S. Winstein, *J. Am. Chem. Soc.*, **80**, 1247 (1958).

(4) S. Winstein, C. Hanson, and E. Grunwald, *ibid.*, **70**, 812 (1948).

(5) Melting points are uncorrected. Oxygen-18 analyses were performed by Analytical Corporation, New York, N. Y., and the Department of Chemistry, Arizona State University, using the procedure of D. Rittenburg and L. Ponticorvo [*Intern. J. Appl. Radiation Isotopes*, **1**, 208 (1956–1957)]. Possible error in O^{18} analysis was estimated as ±3%. Elemental analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.