Notes

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A Convenient Preparation of Difluorodiazine

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Difluorodiazine (N_2F_2) has been known for over two decades but study has been limited by the lack of a suitable preparative method. Previous preparations have been the decomposition (often explosive!) of fluorine azide, FN_3,[1] the electrolysis of ammonium bifluoride (5–10% of the condensable gas mixture),[2] arc or spark activation of a mixture of elemental nitrogen and its higher fluoride (1–3% yield),[3] and the reaction of NF_3 with mercury vapor in an electric discharge (15% yield).[4] The following method gives N_2F_2 in fair and consistent yields with a greatly lessened danger of explosion by reaction of base with the readily prepared difluorourea.

Table I
Difluorodiazine Yield from Difluorourea

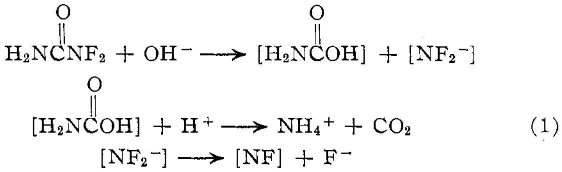
Run	Difluorourea, *M*	Initial temp., °C.	KOH, *M*	Yield,[a] % N_2F_2	Yield,[a] % N_2F_4	Remarks
1	0.98	−20	5.0	19	2	1-min. addn.
2	0.98	−20	5.0	23	4	4-min. addn.
3	0.98	−20	5.0	28	6	12-min. addn.
4	0.98	−20	5.0	27	4	24-min. addn.
5	1.25	−10	4.5	30	12	
6	1.25	−35	4.5	32	21	
7	0.82	−35	4.0	22	6	Partially frozen
8	0.82	−20	4.0	30	8	
9	0.82	0	4.0	27	7	
10–19	1.50	0	4.0	42	N.d.	Av. of 10 runs
20–24	0.87	0	4.0	29	N.d.	Av. of 5 runs
25	0.77	−20	10	35	10	N^{15} urea used
26	0.75	−10	10	34	13	32% NH_4^+ recovered[b] from soln.; 17% NO_2^- or NO_3^- recovered[c]
27	0.18	−10	10	{15	5}	26% NH_4^+; 17% NO_2^-, NO_3
28	0.06	−10	10			26% NH_4^+; 41% NO_2,$^-$ NO_3

[a] Yield based on iodometric titration of difluorourea. [b] Kjeldahl determination. [c] Solution from b treated with Devarda's alloy, followed by a second Kjeldahl.

The aqueous fluorination of urea to N,N-difluorourea was reported by Grakauskas,[5] who also found that the reaction of difluorourea (H_2NCONF_2) with aqueous base did not yield significant amounts of products containing the NF bond. In this work it was found that dilute base at 25° or above does indeed yield only traces of N_2F_2, N_2F_4, and HNF_2; however, lower temperatures and more concentrated base give quite satisfactory N_2F_2 production. Table I indicates the results of a series of reactions in which aqueous base was added dropwise to a stirred, chilled difluorourea solution, the products being swept with helium through a base scrubber, a CO_2 trap, and a N_2 trap (see Experimental Section).

Generally the results can be summarized by the statement that low temperatures and high concentrations favor good yields. However, too low (run 7) a temperature caused slushing of the difluorourea solution, in which case lower yields were found. The time of addition (runs 1–4) seemed to be important mainly as it concerned temperature (the addition of KOH to the strongly acid HF solution causes enough heat evolution to warm the solution above 25°). Runs 5, 6, and 10–19 were with the most concentrated urea and gave yields of N_2F_2. Comparison of runs 5 and 6 and 7, 8, and 9 indicates temperature is not critical if kept between 0 and −30°. Comparison of runs 25 and 26 with 7–9 indicates that increasing the base concentration raises the yield only slightly.

The presumed course of the reaction (1) involves nucleophilic attack of hydroxide ion at carbon ultimately producing "fluoronitrene" or "fluorazene," which then disappears (2) by attack on one of the precursors, dimerization, or hydrolysis. The influence of



$$\mathrm{H_2N\overset{O}{\overset{\|}{C}}NF_2} + \mathrm{OH^-} \longrightarrow [\mathrm{H_2N\overset{O}{\overset{\|}{C}}OH}] + [\mathrm{NF_2^-}]$$
$$[\mathrm{H_2N\overset{O}{\overset{\|}{C}}OH}] + \mathrm{H^+} \longrightarrow \mathrm{NH_4^+} + \mathrm{CO_2} \qquad (1)$$
$$[\mathrm{NF_2^-}] \longrightarrow [\mathrm{NF}] + \mathrm{F^-}$$

concentration and temperature on yield is a result of competitive reactions which give N_2F_2 by coupling and soluble oxidized nitrogen species by hydrolysis. Dilution favors the hydrolysis reaction over the N–N-forming reactions as shown by runs 25 and 26 in Table I.

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(1) J. F. Haller, Ph.D. Thesis, Cornell University, 1942.

(2) C. B. Colburn, F. A. Johnson, A. Kennedy, K. McCallum, L. C. Metzger, and C. O. Parker, *J. Am. Chem. Soc.*, **81**, 6397 (1959).

(3) R. D. Lipscomb, U. S. Patent 2,972,519 (1958).

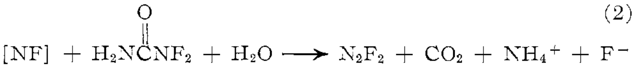
(4) J. W. Frazer, *J. Inorg. Nucl. Chem.*, **11**, 166 (1959).

(5) V. Grakauskas, Abstracts of Papers, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961.

In addition larger proportions of N_2O in the gaseous products were found in runs with more dilute solutions.

$$[NF] + [NF] \longrightarrow N_2F_2$$

$$[NF] + [NF_2^-] \longrightarrow N_2F_2 + F^-$$



$$[NF] + H_2N\overset{\overset{\displaystyle O}{\|}}{C}NF_2 + H_2O \longrightarrow N_2F_2 + CO_2 + NH_4^+ + F^- \qquad (2)$$

$$[NF] + H_2O \longrightarrow HF + [HNO]$$

Evidence for the intermolecular *vs.* the intramolecular formation of N_2F_2 is furnished by the results of the N^{15} runs.[6] These were done with a fluorinated sample of 4.7 mmoles of ordinary urea (0.38% N^{15}) and 45.8 mmoles of enriched urea (34.8% N^{15}). The expected isotopic abundances for intermolecular reaction (31.3% random N^{15} in N_2F_2) and for intramolecular reaction (0.38 + 34.8% N^{15} summed after intramolecular reaction) and the experimental results of mass spectrometric analysis are shown in Table II. The cracking patterns were as expected for the usual 3:1 *trans*:*cis* mixture. The results clearly show that intermolecular reaction is the predominant path and that randomization of N^{15} and N^{14} is complete within the limits of measurement. The mass spectrometric abundance measurements on NF_2 (from N_2F_4[7]) are included to show that no significant selective fluorination of the N^{14}–N^{15} system has occurred.

TABLE II

RELATIVE ABUNDANCE OF ISOTOPIC SPECIES

	N_2F_2		
Parent molecule	$FN^{15}–N^{15}F$	$FN^{15}–N^{14}F$	$FN^{14}–N^{14}F$
Calcd. (0.38 + 34.8%—intra.)	0.110	0.413	0.478
Calcd. (31.3%—inter.)	0.098	0.430	0.472
Found			
$FNNF^+$	0.107 ± 10	0.430 ± 10	0.463 ± 10
FNN^+	0.098 ± 2	0.431 ± 2	0.471 ± 2
Weighted av.	0.099 ± 2	0.431 ± 2	0.470 ± 2
	N_2F_4		
Parent molecule		$N^{15}F_2$	$N^{14}F_2$
Calcd. (31.3% or 0.38 + 34.8)		0.313	0.687
Found			
NF_2^+		0.327 ± 10	0.673 ± 10
NF^+		0.306 ± 10	0.694 ± 10
Av.		0.316 ± 7	0.683 ± 7

Experimental Section

A 250-ml. three-neck flask with standard taper joints was fitted with a gas dispersion tube for sweeping the solution with helium, a pressure-equalizing dropping funnel, and an exit tube. The exit tubing was connected to a second gas dispersion tube which entered a second flask or gas washing bottle containing 5 *N* KOH to ensure removal of HNF_2 and CO_2. The exit tube of the base scrubber led to a trap cooled with liquid nitrogen, then to a water bubbler, and finally was vented to the atmosphere (hood). The reaction flask was kept in a cooling bath and stirred magnetically. All joints were greased with Kel-F 90 grease[8] and fastened to prevent opening by the slight helium back pressure.

The usual procedure was to add 25 ml. of about 1 *N* difluorourea solution to the reaction flask, fasten the dropping funnel, and adjust the cold bath. After the helium purge was well underway, the N_2 dewar was filled slowly. Finally base was added dropwise until the reaction solution no longer gave off bubbles, after which about 30 min. was allowed for a final helium purge. The N_2 trap and contents were transferred to a vacuum line, and the water was separated from N_2F_2, N_2F_4, N_2O, and other volatiles by passage through a CO_2-cooled trap.

Caution.—Difluorodiazine is potentially explosive. When it is mixed with organic compounds, explosions usually result. Personnel should always be protected when working with this compound. The above procedure has proven highly satisfactory in that no explosions were experienced in some 50 runs.

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(6) The difluorodiazine prepared in these runs has been used in the elegant studies of J. D. Baldeschweiler, J. H. Noggle, and C. B. Colburn, *J. Chem. Phys.*, **37**, 182 (1962), and R. L. Kuczcowski and E. B. Wilson, Jr., *ibid.*, **39**, 1030 (1963) to establish unequivocally the "*cis*" and "*trans*" structure of the isomers.

(7) F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, **83**, 3043 (1961).

(8) Trademark of Minnesota Mining and Manufacturing Company, Minneapolis, Minn.

CONTRIBUTION NO. 1842 FROM THE DEPARTMENT
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Improved Methods for the Synthesis of the Cyclic Selenides. Selenacyclopentane, Selenacyclohexane, 1-Oxa-4-selenacyclohexane, and 1-Thia-4-selenacyclohexane

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Previous methods for the synthesis of selenacyclopentane,[1,2] selenacyclohexane,[2,3] 1-oxa-4-selenacyclohexane (1,4-oxaselenane),[4] and 1-thia-4-selenacyclohexane (1,4-thiaselenane)[5,6] involve the preparation and handling of hydrogen selenide as one step. In addition to this unpleasant and time-consuming process, the methods have other undesirable features such as the use of metallic sodium and an atmosphere of hydrogen gas. Although the new methods reported here do not, in general, give improved yields, the procedures are simple, involve fewer hazardous or obnoxious steps, and require only 3–4 hr. for completion. The general procedure is based on the use of sodium formaldehydesulfoxylate (rongalite)[7] and is similar to that used in the synthesis of 1,4-thiatellurane.[8]

Although the mechanisms of the synthetic reactions are not known, the stoichiometry is represented by the equations

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(1) G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1096 (1929).

(2) Y. K. Yur'ev, *J. Gen. Chem. USSR*, **16**, 851 (1946); *Chem. Abstr.*, **41**, 1654*c* (1947).

(3) G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 2197 (1929).

(4) C. S. Gibson and J. D. A. Johnson, *ibid.*, 266 (1931).

(5) C. S. Gibson and J. D. A. Johnson, *ibid.*, 1529 (1933).

(6) J. D. McCullough and P. Radlick, *Inorg. Chem.*, **3**, 924 (1964).

(7) M. L. Bird and F. Challenger, *J. Chem. Soc.*, 570 (1942).

(8) J. D. McCullough, *Inorg. Chem.*, **4**, 862 (1965).