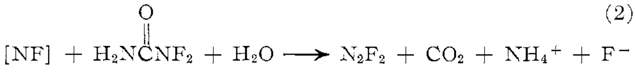
In addition larger proportions of N_2O in the gaseous products were found in runs with more dilute solutions.

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

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

(2)



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

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

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.

Acknowledgment.—The work described herein was carried out under DA-01-021 ORD-11878. The author wishes to thank Dr. C. B. Colburn for his interest in the problem and Dr. C. O. Parker for fluorination of the urea solution.

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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.

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Improved Methods for the Synthesis of the Cyclic Selenides. Selenacyclopentane, Selenacyclohexane, 1-Oxa-4-selenacyclohexane, and 1-Thia-4-selenacyclohexane

BY J. D. MCCULLOUGH AND ALLEN LEFOHN

Received July 22, 1965

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).

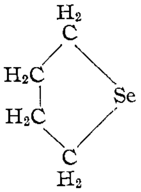
[7] M. L. Bird and F. Challenger, *J. Chem. Soc.*, 570 (1942).

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

$$HOCH_2SO_2^- + Se + 2OH^- = HOCH_2SO_3^- + Se^{2-} + H_2O \quad (1)$$

$$X(CH_2)_4X + Se^{2-} = X(CH_2)_4Se^- + X^- \quad (2)$$

$X(CH_2)_4Se^- =$



$+ X^-$ (3)

The selenides react with the halogens to form crystalline addition compounds, and solutions of the latter in a suitable solvent, such as ethylene chloride, react quantitatively with aqueous potassium iodide with liberation of iodine. For example, the dibromide of selenacyclopentane reacts as follows with iodide ion

$$C_4H_8SeBr_2 + 3I^- = C_4H_8Se + I_3^- + 2Br^- \quad (4)$$

Titration of the resulting iodine with standard thiosulfate permits evaluation of the equivalent weight of the addition compound and thus indicates its purity.[9]

Experimental Section

Ventilation.—Because of the unpleasant odors of the products and the toxicity of mustard gas, the syntheses were carried out in a well-ventilated fume hood.

Materials.—Unless otherwise specified, reagents were of an analyzed grade and solvents were Eastman White Label products.

β,β'-Dichlorodiethyl Sulfide.—Mustard gas was prepared from technical grade thiodiglycol (Matheson Coleman and Bell) by the method of Reeves and Love.[10]

General Synthetic Procedure.—The following quantities of reactants were found satisfactory, but the actual amounts may be varied for convenience as long as the ratios are not changed greatly. Sodium formaldehydesulfoxylate (Eastman practical grade, 90 g. or 0.75 mole), selenium powder (Braun Chemical Co. 99% grade, 25 g. or 0.32-g.-atom), and NaOH pellets (70 g. or 1.75 moles) were mixed in a 2-l., three-necked flask. Water (in the amount specified below for each selenide) was added, and the mixture was brought to reflux for about 15 min. The appropriate organic dihalide (0.32 mole) was then added slowly from a dropping funnel over a period of about 30 min. while gentle reflux was maintained. The apparatus was then modified for steam distillation with a coolant-coil-type condenser and a receiver immersed in an ice–water mixture. Steam distillation was continued until no more oily or solid selenide formed in the condenser. The liquids were collected by means of a separatory funnel and dried over anhydrous $MgSO_4$. For many uses, the liquid selenides are sufficiently pure at this stage. However, since they may contain some unreacted organic halide, purification is recommended as described below. The solid 1,4-thiaselenane was collected by filtration and, after drying, was quite pure.

Optimum Reaction Conditions.—Two types of side reaction compete with the formation of the desired cyclic product. (See discussion in ref. 8.) One is the hydrolytic loss of the organic dihalide; the other is the formation of polymer. In the synthesis of each selenide, the volume of solvent water was varied, and, in three cases, the effect of diluting the organic halide with water was studied. The most satisfactory conditions are specified below for each selenide.

Purification of Liquid Selenides.—If a pure, liquid selenide is required, it is recommended that the oil be converted to the dibromide, recrystallized, reduced back to the selenide, steam distilled, separated, and dried.

Conversion to the dibromide requires some care, as too rapid addition of bromine, or excess bromine, may result in the formation of some perbromide.[1,3] The oil was dissolved in 15–20 times its own weight of carbon tetrachloride. A solution of bromine in carbon tetrachloride (about 2–3 M) was then added dropwise, with thorough mixing, until an amount within 5% of the stoichiometric quantity had been added. The mixture was allowed to cool, and the crystals were collected on a glass filter. The dibromide was next recrystallized, using the solvent and ratio specified below under the individual compounds. Surprisingly, the solubility characteristics of the dibromides are quite different from each other; hence, a single, satisfactory solvent cannot be specified. The crystals were spread in a thin layer on filter paper to permit complete evaporation of solvent as the latter could otherwise be carried along as a contaminant.

Reduction of the dibromides was carried out by refluxing with aqueous sodium metabisulfite. In a typical reduction, 20 g. of dibromide, 72 g. of $Na_2S_2O_5$, and 250 ml. of water were refluxed in a 1-l., three-necked flask. A complex between sulfur dioxide and the selenide formed which gave the mixture a brilliant yellow color. After refluxing 10–15 min., a solution of 30 g. of NaOH in 75 ml. of water was added and the mixture steam distilled as in the general procedure. If the sulfur dioxide was not thus removed, the distilled selenide had a yellow color due to volatility of the components of the complex. When purified by this procedure and dried, the selenides were of high purity as shown by their n.m.r. spectra.[11]

Selenacyclopentane.—Yields of the liquid selenide in this case were 70, 79, 75, and 62%, respectively, when 200, 300, 400, and 800 ml. of water were used without dilution of the 1,4-dibromobutane with ethanol. When the 1,4-dibromobutane was diluted with ethanol (69 g. of dibromobutane in 200 ml. of ethanol), the yield of selenide fell to less than 5% when 400 ml. of water was used.

Selenocyclopentane Dibromide.[1]—This compound crystallized as brilliant yellow needles from methanol. Twelve milliliters of the solvent dissolved 1 g. of the dibromide at the boiling point.

Iodometric Equivalent.[9]—*Anal.* Calcd. for $C_4H_8SeBr_2$: 147.4. Found: 147.3.

Selenacyclohexane.—The yields of liquid selenide were 51, 64, and 50%, respectively, when 300- 400-, and 800-ml. volumes of water were used without dilution of the 1,5-dibromopentane with ethanol. When 400 ml. of water was used, dilution of the 1,5-dibromopentane with 200 ml. of ethanol caused the yield of selenide to drop to 7%.

Selenacyclohexane Dibromide.[3]—This dibromide crystallized satisfactorily as yellow needles from carbon tetrachloride in the ratio of 10 ml. of boiling solvent/g. of dibromide.

Iodometric Equivalent.—*Anal.* Calcd. for $C_5H_{10}SeBr_2$: 154.5. Found: 154.4.

1,4-Oxaselenane.—The yield of this selenide was not greatly affected by the volume of water used, being 30 ± 2% in the range of 400 to 800 ml. The effect of dilution of the β,β'-dichlorodiethyl ether with ethanol was not studied.

1,4-Oxaselenane Dibromide.[4]—Recrystallization from ethylene dichloride (3 ml. of solvent/g. of dibromide) gave yellow needles in good yield.

Iodometric Equivalent.—*Anal.* Calcd. for $C_4H_8OSeBr_2$: 155.4. Found: 155.5.

1,4-Thiaselenane.—When the β,β'-dichlorodiethyl sulfide was not diluted with ethanol, the yield of this selenide was 1.9% in 200 ml. of water and 3.3% in 800 ml. In the latter volume of water, the yield was increased to 5.3% when the mustard gas (50 g.) was dissolved in 400 ml. of ethanol. After drying, the steam-distilled product was of high purity, m.p. 107.5°. However, it may be recrystallized from methanol, or sublimed, if higher purity is required.

Acknowledgment.—The authors are pleased to acknowledge the financial assistance of the National Science Foundation by means of Grant NSF-GP 3408.

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[9] J. D. McCullough, *Inorg. Chem.*, **3**, 1425 (1964).

[10] A. M. Reeves and S. Love, *Science*, **107**, 204 (1948).

[11] M. L. Maddox, Ph.D. Dissertation, University of California at Los Angeles, 1965.