hydroxide solution (40 ml.), and extracted with chloroform. Removal of the chloroform gave a residual gum which was heated under reflux in diethyleneglycol (20 ml.) for 1 hr. The mixture was filtered, the filter washed with methanol, and the combined filtrate diluted with water, extracted with ether, and worked up in the usual way. The product was dissolved in light petroleum–benzene (3:1) and chromatographed on alumina (Merck, acid-washed). Elution with the same solvents (300 ml.) gave an oil (9 mg.) followed by a solid (160 mg.), eluted with the next 600 ml. solvent. Recrystallization of this product from chloroform–methanol gave 2,3-dimethyl-3′,4′,6,7-bismethylenedioxy-1-phenylnaphthalene [dehydroepigalbacin (V)] as prisms, m.p. 171–172°.

Anal. Calcd. for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03; O, 19.98. Found: C, 75.40; H, 5.04; O, 19.63. λ 332 (ε 4900), 325 (2800), 318 (3300), 292 (10,200), 284 (9900), 234 mμ (48,500). λ 3.45, 3.58, 6.20, 6.65, 6.71, 6.85, 7.37, 7.50, 8.1–8.4 (broad), 8.59, 8.90, 9.09, 9.68, 10.5–10.8 (broad), 11.34 μ.

Nuclear Magnetic Resonance Spectra.—All samples were run in deuteriochloroform solution with tetramethylsilane added as an internal reference. The peak positions are relative to this standard and were obtained directly from a Varian A-60 spectrometer. The spectra reproduced in Fig. 1–5 were obtained, however, from Varian HR-60 and HR-100 spectrometers. The chemical shifts were measured in the following manner. For sharp lines, the shifts are rounded off to the nearest c.p.s. and converted to p.p.m. In the case of multiplets, the centers of the appropriate multiplets were located within a c.p.s. and also converted to p.p.m. When higher order perturbation was evident in the intensity distribution of a multiplet, the center of gravity was estimated to the nearest c.p.s. and converted to p.p.m.

Chemistry of Carbon Diselenide.   I.   Reactions with Primary Amines[1]

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Carbon diselenide has been treated with primary amines to give good yields of seleno-2-benzimidazolinone, seleno-2-benzoxazolinone, seleno-2-benzothiazolinone, seleno-2-imidazolidinone, selenotetrahydro-2(1*H*)-pyrimidinone, and several substituted selenoureas. The diselenocarbamate salts and isoselenocyanates appear to be intermediates in the reaction.

Carbon diselenide has been prepared by the reaction of hydrogen selenide with carbon tetrachloride[2,3] and, more satisfactorily, by the reaction of selenium with methylene chloride.[4] In many respects carbon diselenide behaves like carbon disulfide. It reacts with alcohols to form diselenocarbonates,[2,3] with secondary alkyl amines to form diselenocarbamates,[5] and with chlorine to form perchloromethylselenol.[4] However, carbon diselenide differs from carbon disulfide in that it polymerizes readily,[3,5] especially in the presence of ammonia or amines. This polymerizability, along with the disagreeable odor frequently obtained when working with selenium compounds, apparently has discouraged a more complete study of the chemistry of carbon diselenide. However, with the potential commercialization of carbon diselenide in mind, we have undertaken such a study. In our initial work, we have found that carbon diselenide can react smoothly with primary amines to form the expected products. Most of the products reported are new compounds.

Barnard and Woodbridge[5] studied the reaction of carbon diselenide with secondary amines, and found that it was essential to avoid a localized excess of the diselenide in order to prevent polymer formation. By the slow addition of a 10% solution of carbon diselenide in dioxane to an alkaline solution of the secondary amine at −10°, they obtained high yields of dialkyl-diselenocarbamates. The only work previously reported on reactions of carbon diselenide with primary amines is that of Grimm and Metzger[3] who prepared 1,3-diphenylselenourea in low yield by the addition of

a dilute solution of carbon diselenide to an excess of aniline.

We have treated carbon diselenide with aniline in refluxing carbon tetrachloride and obtained 1,3-diphenylselenourea in essentially quantitative yield. The reaction of carbon diselenide with the dibasic *o*-phenylenediamine gave the cyclic selenourea, namely, seleno-2-benzimidazolinone.[6] Reactions with *o*-aminophenol and *o*-aminothiophenol gave the cyclic products, seleno-2-benzoxazolinone and seleno-2-benzothiazolinone, respectively. The primary aliphatic amines, benzylamine, ethylamine, *n*-butylamine, ethylenediamine, and 1,3-diaminopropane also gave analogous products in good yield.

Polymer formation was eliminated by maintaining extremely low concentrations of carbon diselenide in most cases. This was done by slowly adding a dilute solution of carbon diselenide to the vigorously stirred amine solution held usually at about 80° to ensure immediate reaction of the added carbon diselenide. Such precautions were not necessary in reactions with *o*-aminophenol and *o*-aminothiophenol, because these amines were not basic enough to promote polymerization of the carbon diselenide.

The reaction of carbon diselenide with a primary amine apparently proceeds in a manner similar to that of carbon disulfide.[7] Thus, the amine salt of the diselenocarbamate forms first, and, upon heating, decomposes with the evolution of hydrogen selenide and the formation of the isoselenocyanate and amine. The isoselenocyanate then reacts with the amine to form a selenourea.

(1) This work was supported by a research contract with The Selenium and Tellurium Development Committee.
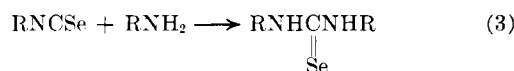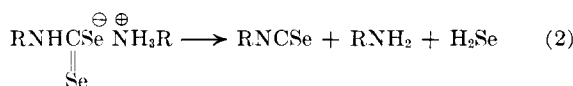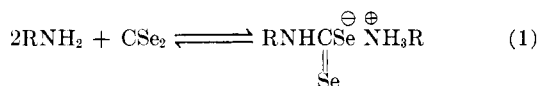
(2) B. Rathke, *Ann.*, **152**, 181 (1869).

(3) H. G. Grimm and H. Metzger, *Ber.*, **69B**, 1356 (1936).

(4) D. J. G. Ives, R. W. Pittman, and W. Wardlaw, *J. Chem. Soc.*, 1080 (1947).

(5) D. Barnard and D. T. Woodbridge, *ibid.*, 2922 (1961).
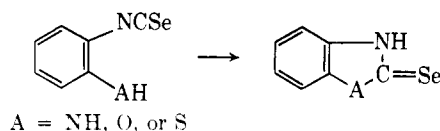
(6) Infrared spectra and n.m.r. spectra were obtained in an attempt to establish the keto-enol equilibria of the products. However, several reference compounds must be studied before a sound interpretation of the spectra can be made. This work, coupled with alkylation studies, is in progress and will be reported later.

(7) D. C. Schroeder, *Chem. Rev.*, **55**, 189 (1955).

$$2RNH_2 + CSe_2 \rightleftharpoons RNH\underset{\underset{Se}{\parallel}}{C}Se^{\ominus}\ \overset{\oplus}{N}H_3R \qquad (1)$$

$$RNH\underset{\underset{Se}{\parallel}}{C}Se^{\ominus}\ \overset{\oplus}{N}H_3R \longrightarrow RNCSe + RNH_2 + H_2Se \qquad (2)$$

$$RNCSe + RNH_2 \longrightarrow RNH\underset{\underset{Se}{\parallel}}{C}NHR \qquad (3)$$

When the primary amine is o-phenylenediamine, o-aminophenol or o-aminothiophenol, the isoselenocyanate intermediate cyclizes intramolecularly through the adjacent amino, hydroxyl, or sulfhydryl group.

(structure: o-disubstituted benzene bearing NCSe and AH groups → cyclized benzo ring with NH–C=Se, A)

A = NH, O, or S

Evidence in support of the previous sequence was obtained by the preparation of a mixed selenourea using an amine in step 3 that was different from that used in step 1. The diselenocarbamate salt formed from benzylamine at room temperature was treated with a large excess of diethylamine and refluxed overnight. A nearly quantitative yield of 1,1-diethyl-3-benzylselenourea resulted.

In all cases good yields of product were obtained if the reactions were stopped as soon as hydrogen selenide evolution subsided. The over-all rate-determining step, therefore, appears to be either step 1 or step 2. When an aliphatic amine was used, there was no polymer formation even at room temperature; however, prolonged heating was necessary to complete the evolution of hydrogen selenide. Therefore, with aliphatic amines step 1 is rapid (no carbon diselenide accumulates to undergo polymerization) and step 2 must be the rate-determining step. With aromatic amines, such as aniline or o-phenylenediamine step 1 was much slower (heating was necessary to prevent polymer formation), and step 2 was much faster (hydrogen selenide evolution subsided in less than an hour after the last carbon diselenide was added).

The diselenocarbamate salt intermediates were found to be extremely susceptible to air oxidation which resulted in the formation of red or black elemental selenium. All reaction mixtures were protected from air by nitrogen until hydrogen selenide evolution was completed.

The selenoureas and related products obtained are given in Table I. They are colorless, crystalline, and practically odorless solids which melt with decomposition in the presence of air. They have been stored in closed containers at 0° for several months with no apparent decomposition. In the presence of air at room temperature or in solvents containing dissolved oxygen, they gradually darken, presumably from the formation of elemental selenium. The 1,3-diethylselenourea is particularly sensitive to air. Work on the isolation of oxidation products is in progress.

TABLE I

REACTIONS OF CARBON DISELENIDE WITH PRIMARY AMINES

Product	Reactant	Moles of reactant[a]	Reflux time, hr.	M.p., °C.[b]	Yield, %	Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found	Se, %[n] Calcd.	Se, %[n] Found
1,3-Diphenylselenourea	Aniline	0.05	1.5[c,d]	190–192 dec[j,k]	98	$C_{13}H_{12}N_2Se$	...	...	...	...	...	...	...	...
1,3-Dibenzylselenourea	Benzylamine	.05	5[c,e]	182–183[k]	93	$C_{15}H_{16}N_2Se$	59.4	59.4	5.3	5.3	9.2	9.4	26.1	25.6
1,3-Diethylselenourea	Ethylamine	.10	21[c,f,g]	94–95[l]	73	$C_5H_{12}N_2Se$	33.5	33.6	6.7	6.6	15.6	15.7	44.2	44.0
1,3-Di-n-butylselenourea	n-Butylamine	.05	21[c,f]	73–74.5[l]	67	$C_9H_{20}N_2Se$	45.9	46.0	8.5	8.5	11.9	12.0	33.7	33.6
Selenotetrahydro-2(1H)-pyrimidinone	1,3-Diaminopropane	.01	21[f,h]	224–226 dec.[k]	66	$C_4H_8N_2Se$	29.4	29.6	4.9	5.0	17.2	17.1	48.5	48.4
Seleno-2-imidazolidinone	Ethylenediamine	.01	21[f,h]	234–236 dec.[k]	79	$C_3H_6N_2Se$	24.2	24.2	4.0	3.8	18.8	19.0	53.0	53.3
Seleno-2-benzimidazolinone	o-Phenylenediamine	.005	2[c,d]	234–236 dec.[l]	85	$C_7H_6N_2Se$	42.7	42.4	3.0	3.2	14.2	14.2	40.1	40.3
Seleno-2-benzoxazolinone	o-Aminophenol	.004	16[c,i]	201–203 dec.[l]	78	C_7H_5NOSe	42.4	42.5	2.5	2.6	7.1	7.0	39.9	40.1
Seleno-2-benzothiazolinone	o-Aminothiophenol	.004	24[c,i]	173–174[l]	62	C_7H_5NSSe	39.3	39.4	2.3	2.7	6.5	6.7	36.9	37.0
1,1-Diethyl-3-benzylselenourea	Benzylamine + diethylamine	.015 + .50	16[e]	93–94[m]	96	$C_{12}H_{18}N_2Se$	53.5	53.3	6.7	6.8	10.4	10.4	29.4	29.4

[a] The amount of carbon diselenide used was 0.005 mole in each case. [b] All melting points are uncorrected. [c] Includes 1-hr. addition time under reflux. [d] The solvent was CCl₄. [e] The solvent was benzene. [f] Includes 1-hr. addition time at room temperature. [g] Some of the ethylammonium N-ethyldiselenocarbamate intermediate sublimed into the reflux condenser and formed colorless needles; they were water soluble and turned red and black very rapidly when exposed to air. [h] The solvent was ethanol. [i] The carbon diselenide was added all at once. [j] C. Hasan and R. F. Hunter, J. Chem. Soc., 1762 (1935), m.p. 192–194°. [k] Recrystallized from ethanol. [l] Recrystallized from benzene. [m] Recrystallized from a benzene–hexane mixture. [n] Selenium was determined by peroxide decomposition in a Parr bomb followed by reduction with hydroxylamine hydrochloride and 8 N HCl saturated with SO₂. Sample quantities sufficient to give 50–100 mg. of elemental selenium were used.

Experimental

The carbon diselenide used initially in this work was prepared in this laboratory by the method of Ives, et al.[4] Subsequently, experimental quantities of carbon diselenide were obtained from Noranda Research Centre, Pointe Claire, Quebec.

It has been our experience that redistilled carbon diselenide has an odor very similar to that of carbon disulfide. However, when carbon diselenide vaporizes and becomes mixed with air, extremely repulsive stenches are gradually formed. Many of the reaction residues gave foul odors that were rather persistent. By using an effective hood and working with rather small quantities of materials, as well as using a charcoal trap, Dry Ice trap, or a potassium hydroxide decontamination bath whenever it seemed advisable, pleasant working conditions were maintained.

It should be noted that some of the volatile selenium compounds produced may be extremely toxic as well as foul. For example, hydrogen selenide, a by-product of the reactions described, is about as toxic as hydrogen cyanide. An effective hood, therefore, is essential from a safety standpoint and a trap containing caustic solution is advisable, especially when larger quantities are involved.

1,3-Diphenylselenourea.—A solution of 0.32 ml. (0.005 mole) of carbon diselenide in 100 ml. of carbon tetrachloride was added dropwise over a 1-hr. period with stirring to a refluxing solution of 4.6 ml. (0.05 mole) of aniline in 50 ml. of carbon tetrachloride. The refluxing was continued 30 min. longer, whereupon hydrogen selenide evolution could no longer be detected by moistened lead acetate paper. A stream of nitrogen was passed through the reaction mixture during the entire period. At the end of the reflux period, the mixture was cooled and filtered to give 1.36 g. (98%) of 1,3-diphenylselenourea, m.p. 190–192° dec. The product was colored pale gray from a trace of elemental selenium. Recrystallization from ethanol, using a stream of nitrogen to displace air, gave a colorless product with no increase in melting point.

Modifications of the above procedure for the preparation of other products are given in Table I. Small amounts of black elemental selenium were sometimes removed by filtering the hot reaction mixtures. In some cases the solutions were concentrated on a rotating evaporator and taken up in the recrystallization solvent in order to obtain crystalline products.

Seleno-2-benzoxazolinone.—A mixture of 0.32 ml. (0.005 mole) of carbon diselenide and 0.44 g. (0.004 mole) of o-aminophenol in 100 ml. of benzene was refluxed with stirring under nitrogen for 16 hr. The mixture was filtered while hot to remove a small amount of insoluble impurities. The filtrate upon cooling yielded 0.48 g. of nearly colorless needles, m.p. 198–200° dec. Concentration of the mother liquors to 25 ml. yielded an additional 0.14 g., m.p. 194–196° dec. The total yield was 78%. Recrystallization of the product from benzene gave colorless needles, m.p. 201–203° dec.

Seleno-2-benzothiazolinone was prepared similarly.

1,1-Diethyl-3-benzylselenourea.—A solution of 0.32 ml. (0.005 mole) of carbon diselenide in 50 ml. of benzene was added dropwise over a 20-min. period with stirring to 1.6 ml. (0.015 mole) of benzylamine in 100 ml. of benzene at room temperature under nitrogen. A solution of 51.5 ml. (0.50 mole) of diethylamine in 100 ml. of benzene was then added over a 15-min. period with stirring at room temperature. After the addition was complete, the mixture was refluxed for 16 hr. The resulting dark brown mixture was concentrated to a sirup, redissolved in 100 ml. of benzene, and filtered to remove a small amount of black precipitate. The clear yellow filtrate was washed with 60 ml. of 0.2 N hydrochloric acid followed by three washings with 50 ml. of distilled water. The benzene layer was dried over anhydrous magnesium sulfate, concentrated to a sirup, and cooled. Filtration followed by washing with a benzene–pentane mixture gave 1.15 g. of 1,1-diethyl-3-benzylselenourea as pale yellow needles, m.p. 62–67°. A second crop of 0.15 g., m.p. 65–68°, was obtained by the addition of pentane to the mother liquor. The total yield was 96%. Recrystallization of the first crop from a benzene–hexane mixture gave 0.91 g., fine colorless needles, m.p. 93–94°, that was used as an analytical sample.

The Claisen Rearrangement of Allyl Ethers of α-Hydroxybenzalacetophenones[1]

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The allyl ethers of several phenylbenzylglyoxals have been prepared and rearranged to the corresponding C-allyl glyoxals. The electron-donating CH_3–O– group in the o- and p-position of the benzyl nucleus promotes the rearrangement, whereas the similarly placed electron-withdrawing NO_2– group retards the rearrangement.

The Claisen rearrangement has been shown to be intramolecular,[3-6] and the kinetics of the reaction have been established as first order.[7] Studies of a series of p-X-phenyl ethers[8] and p-X-cinnamyl phenyl ethers[9] indicate that both the aryloxy and allyl groups assume partial radical character in the transition state.

While the allyl ethers of the enolic modification of β-diketones have been subjected to the Claisen rearrangement, those of the α-diketones have not. Since the allyl ethers of the α-diketones possess the structural requirements necessary for this rearrangement, one might expect them to rearrange.

In order to test this hypothesis, the chalcones (I–VII) were prepared by condensing the appropriate aldehyde and acetophenone. The chalcones were converted to the corresponding oxides (VIII–XIV). Oxide (VIII) was converted to the glyoxal (XV) by way of the chlorohydrin; oxides (IX–XIV) were isomerized with alkali to the diketones (XVI–XXI). These glyoxals in turn were treated in acetone solution in the presence of potassium carbonate with allyl bromide, yielding the allyl ethers (XXII–XXVIII), which were subjected to the conditions of rearrangement (p. 1645).

The ethers were refluxed in N,N-dimethylaniline in an atmosphere of nitrogen for twenty-four hours. The extent to which rearrangement occurred is

XXII	⟶ XXIX	18%
XXIII	⟶ XXX	20
XXIV	⟶ XXXI	75
XXV	⟶ XXXII	80
XXVI	⟶ XXXIII	0
XXVII	⟶ XXXIV	0
XXVIII	⟶ XXXV	60

(1) This work was supported by a grant from Research Corporation of New York.

(2) In partial fulfillment of the requirements for the Ph.D. degree.

(3) C. Hurd and L. Schmerling, *J. Am. Chem. Soc.*, **59**, 107 (1937).

(4) A. S. Semenow and J. D. Roberts, *J. Chem. Educ.*, **33**, 2 (1956).

(5) J. P. Ryan and P. R. O'Connor, *J. Am. Chem. Soc.*, **74**, 5866 (1952).

(6) Y. Docker, *Proc. Chem. Soc.*, 141 (1961).

(7) J. Kincaid and D. Tarbell, *J. Am. Chem. Soc.*, **61**, 3085 (1939).

(8) H. Goering and R. Jacobson, *ibid.*, **80**, 3277 (1958).

(9)(a) W. Fife and W. White, 138th National Meeting of American Chemical Society, New York, N. Y., September, 1960, Abstracts of Papers, p. 86; (b) W. White, et al., *J. Org. Chem.*, **26**, 627 (1961).