magnesium iodide in diethyl ether, there was obtained a 60% yield of N^2-*tert*-butyl-N^1-phenyl-2-methylbutanamidine (**6ca**). The results of the amidine synthesis are given in Table III. Characterization data are recorded in microfilm supplement pages. The synthesis of amidines **6** from ketenimines, produced in situ as described above, demonstrates the usefulness of this facile and rapid method. Trialkylketenimines **2** can now be synthesized on a large scale without the necessity of distillation, since the ethereal solution can be used directly for further reactions.

Experimental Section

α-Cyano enamines **1** were prepared as previously described.[6,7] The following preparation serves as an example for the transformation of an α-cyano enamine into the corresponding ketenimine.

Synthesis of Trialkylketenimines 2. In a typical experiment, a solution of 18.0 g (0.1 mol) of 2-*tert*-butylamino-3-ethyl-2-pentenenitrile (**1e**) ($R_1 = R_2 = Et$; R = *t*-Bu) in 20 mL of dry diethyl ether was added dropwise to a freshly prepared solution of methylmagnesium iodide in 130 mL of dry diethyl ether (prepared from 4.2 g (0.175 mol) of magnesium curlings and 24.8 g (0.175 mol) of methyl iodide). After a few minutes an amorphous precipitate (or resinous material) was formed and the mixture was refluxed for 2 h. After cooling to ice-bath temperature the reaction mixture was cautiously triturated with about 75 mL of ice–water and 75 mL of ice-cold saturated aqueous ammonium chloride solution. When the precipitate was decomposed completely, i.e., when homogenous layers were obtained, the ethereal layer was separated, ice was added, and the aqueous layer was twice extracted with ether. Drying of the combined extracts (1 h; $MgSO_4$/K_2CO_3) at ice-bath temperature and evaporation in vacuo at low temperature afforded an oil which was distilled in vacuo using a 10-cm Vigreux column to give 8.1 g of *N*-*tert*-butyldiethylketenimine (**2e**) as a colorless liquid, bp 72 °C (19 mmHg) (yield 53%). In some batches a small amount (1–3%) of *N*-*tert*-butyl-2-ethylbutanamide (**4e**) was present in the distilled product, probably due to capture of moisture during the distillation procedure.

Reaction of Trialkylketenimines 2 with Primary Amines. Typical Procedure. An equimolecular amount of ketenimine **2** and aromatic amine in dry benzene (10% solution) was refluxed for a time indicated in Table III. Evaporation of the solvent in vacuo left an oil which was distilled or analyzed by VPC. In the case of aliphatic amines, a fourfold molar excess was used.

Preparation of Amidines 6 without Isolating Ketenimines 2. The preparation of N^2-*tert*-butyl-N^1-phenyl-2-methylbutanamidine (**6ca**) serves as a typical procedure. The reaction mixture starting from 8.3 g (0.05 mol) of 2-*tert*-butylamino-3-methyl-2-pentenenitrile (**1c**) and 0.0875 mol of methylmagnesium iodide in diethyl ether was triturated with aqueous ammonium chloride as described above. The combined ethereal extracts were dried (1 h; $MgSO_4$/K_2CO_3). After filtration, 4.65 g (0.05 mol) of aniline was added and ether was evaporated in vacuo at low temperature, after which 80 mL of dry benzene was added. This benzene solution was refluxed for 4 h and evaporated to leave an oil, which was distilled in vacuo. The forerun contained mainly aniline and the fraction (6.9 g; yield 60%) boiling at 93–98 °C (0.02 mmHg) was identified as N^2-*tert*-butyl-N^1-phenyl-2-methylbutanamidine (**6ca**). Compound **6ca** solidified on standing, mp 59–61 °C.

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Registry No.—**1a,** 63364-14-7; **1b,** 66102-53-2; **1c,** 66102-54-3; **1d,** 66102-55-4; **1e,** 63364-26-1; benzenamine, 62-53-3; 4-methylbenzenamine, 106-49-0; 4-methoxybenzenamine, 104-94-9.

Supplementary Material Available: Full IR, NMR, and MS data of N^1,N^2-disubstituted alkanamidines **6,** Table IV (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) "Aangesteld Navorser" of the Belgian "Nationaal Fonds voor Wetenschappelijk Onderzoek".
(2) (a) G. R. Krow, *Angew. Chem.*, **83,** 455 (1971); *Angew. Chem., Int. Ed. Engl.*, **7,** 435 (1971); (b) C. L. Stevens and J. C. French, *J. Am. Chem. Soc.*, **76,** 4398 (1954).
(3) W. Ried and P. Junker, *Justus Liebigs Ann. Chem.*, **713,** 119 (1968).
(4) L. A. Singer and G. A. Davis, *J. Am. Chem. Soc.*, **89,** 598 (1967).
(5) T. Kataoka, T. Yasumoto, and E. Naito, Japanese Patent 5111 (1967) (Cl.26C3), March 2, Appl. Nov. 1, 1963; *Chem. Abstr.*, **67,** 100572 (1967).
(6) N. De Kimpe, R. Verhé, L. De Buyck, H. Hasma, and N. Schamp, *Tetrahedron*, **32,** 2457 (1976).
(7) N. De Kimpe, R. Verhé, L. De Buyck, H. Hasma, and N. Schamp, *Tetrahedron*, **32,** 3063 (1976).
(8) For an excellent review concerning the reactivity of α-halo enamines and ketenimmonium salts see L. Ghosez and J. Marchand-Brynaert in "Advances in Organic Chemistry", E. Taylor, Ed., Interscience, New York, N.Y., 1976, p 421.
(9) α-Cyano enamines **1** isomerized partially into imidoylcyanides **3** on gas chromatographic analysis.[7] Since both isomers **1** and **3** could be isolated in pure form by preparative GLC it is more appropriate to refer to them as desmotropic forms. Strong bases can also partly convert α-cyano enamines **1** into imidoylcyanides **3.** The latter conversion was encountered when compounds **1** were allowed to react with KO-*t*-Bu–$CHCl_3$–pentane in order to obtain cyclopropanation (unpublished results).
(10) C. L. Stevens, R. C. Freeman, and K. Noll, *J. Org. Chem.*, **30,** 3718 (1965).
(11) When volatile amines such as isopropylamine were used, the amine was added to the ketenimine after evaporation of ether.

Synthesis of Symmetrical Diselenides from Aliphatic and Aromatic Aldehydes

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An efficient synthetic procedure that gives high yields of symmetric diselenides from aldehydes has been developed. The reaction of H_2Se with aromatic and aliphatic aldehydes in the presence of amines and $NaBH_4$ yields benzylic and aliphatic diselenides. A variant of this synthesis avoids the handling of toxic H_2Se and involves the reaction of NaHSe with amine hydrochloride and aldehyde, followed by a $NaBH_4$ reduction. Specifically deuterium-labeled benzyl diselenide was prepared and a reaction mechanism is proposed.

Many laboratory methods for the preparation of organic diselenides are based on the displacement of halides or tosylates by nucleophilic selenium species.[1] However, there are essentially no direct or efficient methods to convert other common organic functional groups into diselenides. Among potentially attractive new starting materials for such syntheses are carbonyl compounds, and their reactions with hydrogen selenide and its salts have been explored under a variety of conditions in several isolated examples.

Margolis and Pittman[2] obtained low yields of diselenides

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Table I. Reactions of Aromatic Aldehydes with Hydrogen Selenide

Expt no.	Reactant, mmol	Piperidine, mmol	Reaction time, min	$NaBH_4$, mmol	Diselenide yield, %
1	Benzaldehyde (47)	50	10	12	84
2	Benzaldehyde (47)	0	10	12	41
3	Benzaldehyde (47)	5	10	12	42
4	Benzaldehyde (47)	5	3 days	12	88
5	Benzylidenedipiperidine (23.2)	—	10	12	78
6	*p*-Methylbenzaldehyde (50)	50	10	13	85

when the corresponding ketones were treated with excess hydrogen selenide in the presence of strong hydrochloric acid.

3-Formylindole, when reacted with ammonium selenide, also gave a low (38%) yield of di(3-indolylmethyl) diselenide[3] under relatively basic conditions, in analogy to the conversion of aromatic ketones and aldehydes to disulfides[4-7] by alcoholic ammonium sulfides.

The conversion of benzaldehyde to dibenzyl diselenide has also been observed in its reaction with bis(methoxymagnesium) diselenide[8] in the presence of morpholine. It is interesting to note that no diselenide was isolated in the absence of amine.

The synthesis of various diselenides by a similar amine-catalyzed reaction of carbonyl compounds with hydrogen selenide has recently been described.[9]

These reactions appeared quite reasonable, and yet their combined processes did not constitute an efficient and generally applicable synthetic method. In all these examples rather inefficient use is made of the hydrogen selenide or its salts, much of it serving as a reducing agent. Further, long reaction times are required and the products tend to be heavily contaminated with elemental selenium and with oligoselenides. The latter are difficult to remove from the desired diselenides and suffer from slow decomposition with liberation of selenium upon storage and handling.

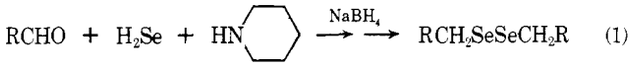
In a preliminary communication[10] we reported a novel synthetic procedure for preparing diselenides from aldehydes where short reaction times produce excellent diselenide yields with high product purity. We found that aromatic and aliphatic aldehydes are readily converted to diselenides by using a two-step, one-pot synthesis involving (a) the interaction of aldehyde, an amine, and hydrogen selenide and (b) treatment of the reaction mixture with sodium borohydride. A convenient variant of the procedure employs sodium hydrogen selenide and an amine hydrochloride to avoid the handling of toxic hydrogen selenide gas.

In this report we document the experimental findings, extend the reaction to the synthesis of a specifically deuterium-labeled diselenide, and propose a reaction mechanism.

Results and Discussion

The conversion of organic aldehydes by reaction with hydrogen selenide and sodium hydrogen selenide in ethanol solution to the corresponding organic diselenides was studied utilizing benzaldehyde as the model compound. Determination of product yields then allowed assessment of the efficiency of the reaction.

Reactions with Hydrogen Selenide. When a slight excess of hydrogen selenide was passed into a solution of benzaldehyde in the presence of 1 molar equiv of piperidine or morpholine in absolute ethanol (expt 1) the solution rapidly turned brown in an exothermic reaction. After 10 min this mixture was treated with sufficient sodium borohydride to give a clear, orange-yellow solution. Addition of water and crystallization of the precipitate gave yellow benzyl diselenide in yields exceeding 80% (eq 1). In the absence of amine, di-



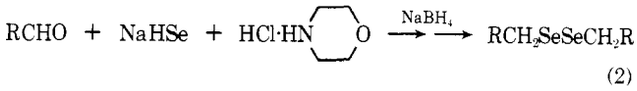
$$\mathrm{RCHO} + \mathrm{H_2Se} + \mathrm{HN}\langle\ \rangle \xrightarrow{\mathrm{NaBH_4}} \mathrm{RCH_2SeSeCH_2R} \quad (1)$$

selenide yields were drastically reduced (expt 2), suggesting that amines must play a major role in the conversion of aldehydes to organic diselenides. The generality of this observation was demonstrated by varying amine concentrations and reaction conditions. Results summarized in Table I show that with only 0.1 molar equiv of piperidine the reaction required 3 days to give yields of diselenide in the 80% range (expt 4). With a 0.1 molar equiv of piperidine we could not exceed a 42% yield after 10 min (expt 3), comparable to what was obtained in the absence of amine. In a similar manner, *N,N'*-benzylidenedipiperidine, an aminal prepared from benzaldehyde and 2 equiv of piperidine,[11] reacted to give 80% benzyl diselenide (expt 5). These results confirm that the amine catalyzes the reactions, probably through the intermediacy of an aminal.

When the sodium borohydride reduction was omitted, diselenide quality and yields were considerably reduced. Since sodium borohydride also reduces diselenides,[12,13] the optimum quantity of this reagent was determined empirically. It was found that 0.25 molar equiv as compared to the aldehyde starting material gave maximum yields of diselenide with little contamination by selenols.

Although an effective reagent, hydrogen selenide gas suffers from the disadvantage of being extremely toxic[14] and its handling must be carefully controlled. Therefore, another approach was developed such that the use of hydrogen selenide gas was avoided.

Reactions with Sodium Hydrogen Selenide. Sodium hydrogen selenide (1.27 equiv), prepared by sodium borohydride reduction of elemental selenium in absolute ethanol,[15] was combined under an atmosphere of nitrogen with 1 equiv each of benzaldehyde and either piperidine hydrochloride or morpholine hydrochloride. Upon heating to reflux a reddish brown solution, similar in appearance to that in the hydrogen selenide reaction, was obtained. Treatment with 0.25 molar equiv of sodium borohydride gave benzyl diselenide in 86% yield, comparable to those in the hydrogen selenide case. Use of this general procedure has led to the synthesis of bis(4,4'-*N,N'*-diethylaminobenzyl) diselenide·2HCl (67%), bis(1-naphthylmethyl) diselenide (92%), bis(2-naphthylmethyl) diselenide (91%), bis(9-anthrylmethyl) diselenide (90%), and bis(1-dodecyl) diselenide (73%) from the corresponding aldehydes (eq 2).



$$\mathrm{RCHO} + \mathrm{NaHSe} + \mathrm{HCl{\cdot}HN}\langle\ \rangle\mathrm{O} \xrightarrow{\mathrm{NaBH_4}} \mathrm{RCH_2SeSeCH_2R} \quad (2)$$

When piperidine (Table II, expt 7) was substituted for the piperidine hydrochloride (Table II, expt 8), the yields were drastically reduced to the 10–15% range. This suggests that the addition of an acid to the sodium hydrogen selenide reaction is essential.

Product yields were optimized following successive modi-

Table II. Reactions of Benzaldehyde with Sodium Hydrogen Selenide

Expt no.	Reactant, mmol	NaHSe, mmol	Amine, mmol	Reaction Time, min	Temp, °C	$NaBH_4$, mmol	Benzyl diselenide yield, %
7	Benzaldehyde (47)	50	Piperidine (50)	20	78	12	13
8	Benzaldehyde (47)	60	Piperidine·HCl (50)	20	78	12	68
9	Benzaldehyde (47)	75	Piperidine·HCl (50)	20	78	12	76
10	Benzaldehyde (47)	75	Piperidine·HCl (50)	45	55–60	12	81
11	Benzaldehyde (47)	75	Piperidine·HCl (50)	60	78	12	83
12	Benzaldehyde (47)	60	Piperidine·HCl (50)	60	78	12	80
13	Benzaldehyde (47)	60	Morpholine·HCl (50)	60	78	12	86
14	Benzaldehyde (12.3)	15	Morpholine·HCl (13)	60	25	3.6	67
15	Benzaldehyde (12.3)	15	Morpholine·HCl (13)	120	25	3.6	74
16	Benzaldehyde (47)	50	Morpholine·HCl (50)	60	78	—	54
17	*N,N'*-Benzylidenedimorpholine (50)	50[a]	—	60	78	—	56
18	*N,N'*-Benzylidenedimorpholine (50)	70[a]	—	60	78	—	82

[a] Hydrochloric acid (100 mmol) was added to the reaction after heating.

Table III. Reactions of Benzaldehyde with Sodium Hydrogen Selenide Using Various Amine Salts

Reactant	Amine salt	Benzyl diselenide yield, %
PhCHO	Ammonium chloride	20
PhCHO	Ammonium chloride	20
PhCHO	Cyclohexylamine·HCl	73
PhCHO	Piperidine·HCl	80
PhCHO	Morpholine·HCl	86
PhCHO	Triethylamine·HCl	64

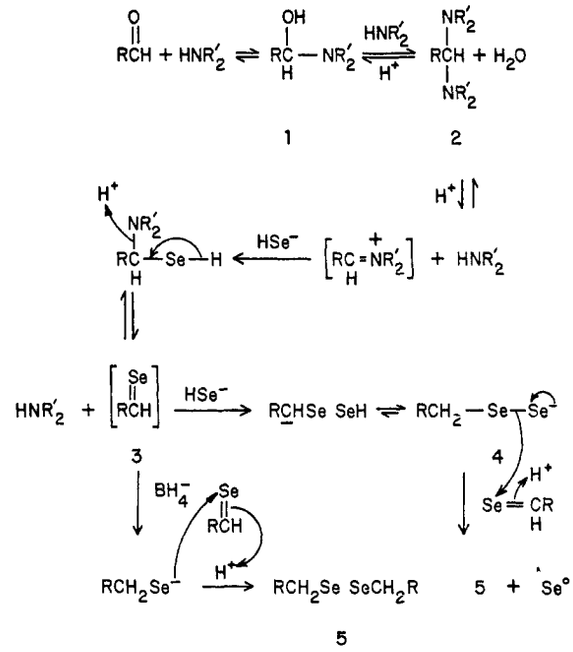
fications in reaction temperatures and reagent concentrations as described in Table II. When the reaction time was increased from 20 min to 1 h at 78 °C (expt 9–12), diselenide yields increased from 68% to more than 80% of theory. An overall yield of 74% was also obtained when sodium hydrogen selenide reacted with benzaldehyde and morpholine hydrochloride at room temperature (expt 14 and 15) for 2 h. These results indicated that, given an appropriate reaction period, satisfactory yields of diselenide may be obtained employing a wide range of reaction temperatures.

The effect of various amines on yields of benzyl diselenide was next investigated (Table III). It was found that secondary amines, i.e., piperidine and morpholine (expt 12 and 13), gave maximum yields of diselenide while decreased yields were obtained with both primary and tertiary amines. Secondary amines and aromatic aldehydes react readily to form hemiaminals and aminals[16] while primary amines yield imines and tertiary amines do not form stable adducts.[17] Thus, the primary step in amine catalysis is assumed to involve formation of secondary amine–aldehyde adducts. Further, our experiments also suggest that favorable reaction conditions are determined by a broad but definite pH range, where either high or low pH extremes decrease reaction rates.

When benzaldehyde was reacted with 1 molar equiv of sodium hydrogen selenide and morpholine hydrochloride with omission of the final sodium borohydride reduction, a 54% yield of benzyl diselenide was obtained (expt 16). This experiment shows that some degree of reduction must occur even in the absence of the final borohydride treatment, possibly by the hydrogen selenide anion. That such a process may be occurring is not surprising in view of reports substantiating the reducing potentials of hydrogen selenide anions.[18]

In order to determine the effectiveness of sodium hydrogen selenide as a reducing species, *N,N'*-benzylidenedimorpholine[19] was reacted with 1.0 and 1.4 molar equiv of sodium hydrogen selenide, respectively, in the presence of 2.0 equiv of

Scheme I



hydrogen chloride (expt 17 and 18). As summarized in Table II, the 1 molar equiv of sodium hydrogen selenide gave a 56% yield whereas the 1.5 molar equiv gave 82% yield, comparable to that obtained with borohydride reduction. The inefficiency of this reaction with 1 molar equiv of sodium hydrogen selenide in the absence of sodium borohydride is the direct result of its dual role as reactant and reducing agent. With sufficient additional reducing agents, such as sodium borohydride, a single molar quantity of sodium hydrogen selenide adequately functions in the conversion of aldehydes to diselenides.

Based upon these experimental results, we propose a mechanistic pathway for this reaction as outlined in Scheme I. In this sequence, the initial reaction involves the formation of an amine–aldehyde adduct such as a hemiaminal or aminal **1** or **2**. Nucleophilic displacement by the hydrogen selenide anion on **1** or **2** followed by an intramolecular elimination leads to a short-lived selenoaldehyde intermediate **3**. In this reaction sequence, we are suggesting two displacement steps, each of which is separately well documented: oxygen is displaced by nitrogen, and nitrogen, in turn, by selenium. The latter reaction is exemplified by formation of 2-selenophthalide from the corresponding imino ester.[20]

The proposed selenoaldehyde intermediate **3**, although never isolated, has previously been postulated as a transient

species in several reactions.[3,21,22] In light of the recent report on a selenoketone,[23] which gave the corresponding diselenide upon reduction with sodium borohydride, the intermediacy of a selenoaldehyde appears reasonable. The absence of selenoaldehyde polymers[24] also indicates that reduction of the postulated intermediate must occur at an exceedingly rapid rate.

Furthermore, we propose that this reduction of the selenoaldehyde **3** involves initial selenophilic attack by the hydrogen selenide anion, forming the diselenol anion **4.** The intermediate **4** could then interact with **3** in a four-centered process analogous to that proposed for the reaction of organic thiosulfates with sodium hydrogen selenide.[18] Upon protonation of the carbanion, the diselenide **5** and elemental selenium are obtained. As elemental selenium is produced, it may interact with unreacted NaHSe to produce the di- or polyselenide anion. That such a process occurs is indicated by the development of an intense red-brown color (characteristic of polyselenide anions) shortly after the reaction starts. This interaction would render the sodium hydrogen selenide less active in the addition and reduction process. However, the hydrogen selenide thus bound may be regenerated by acidification which then reduces the competing loss of sodium hydrogen selenide.[18]

The function of sodium borohydride in the final step involves an alternate reduction mechanism occurring via a hydride addition to the carbon atom of **3,** giving the diselenide **5.** In addition, the final sodium borohydride reduction step also serves as a means of eliminating any trace amounts of selenium by reduction to sodium hydrogen selenide which allows isolation of the precipitated diselenide in clean form.

An alternative and less efficient process which gives small yields of diselenide even in the absence of amines would involve direct nucleophilic attack by the selenide ion on the aldehyde carbonyl. Although the selenide ion is known to be an excellent nucleophile,[4,25] it also behaves as a generally good leaving group.[26,27] Therefore, the direct displacement of oxygen by the selenide anion seems to be difficult and this alternative route appears less attractive than that shown in Scheme I.

This reaction of organic aldehydes with a hydrogen selenide anion in the presence of an amine catalyst introduces an attractive and direct method for obtaining diselenides. The application of this reaction to form deuterium-labeled organic diselenides has also been demonstrated. Using sodium borodeuteride, DCl, ethanol-1-*d*, and benzaldehyde the deuterium-labeled dibenzyl-α-α'-d_2 diselenide was isolated in 54% yields. The potential use of labeled organic diselenides for mechanistic and biochemical studies appears attractive. Application of this synthesis to other similar starting materials is presently being investigated.

Experimental Section

Melting points were determined on a Hoover capillary melting point apparatus and are uncorrected. NMR spectra were obtained on a JEOL C-60H using Me_4Si as an internal standard. A Perkin-Elmer 267 grating spectrophotometer was used to determine infrared spectra. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. 37921.

Benzyl Diselenide Method I. a. Hydrogen selenide from a lecture bottle was slowly passed into a magnetically stirred solution of benzaldehyde (5.0 g, 47 mmol) and piperidine (4.3 g, 50.4 mmol) in absolute ethanol (70 mL). After 10 min a hot, reddish-brown solution had resulted. To this was added sodium borohydride (0.45 g, 12 mmol) in small quantities. The vigorous reaction resulted in a turbid orange-yellow solution. Addition of water precipitated a yellow solid which was collected, washed rapidly with large amounts of water, and dried. Recrystallization from ethanol gave yellow benzyl diselenide (6.7 g, 84%, mp 91–93 °C; lit.[15] mp 92–94 °C): NMR ($CDCl_3$) δ 3.76 (s, 2, $-CH_2-$), 7.18 (s, 5, C_6H_5). The results of varying reaction times and amine concentrations on benzyl diselenide yields using this procedure are summarized in Table I.

b. Hydrogen selenide was gently bubbled into a stirred solution of *N,N'*-benzylidenedipiperidine[11] (6.0 g, 32.2 mmol) in absolute ethanol (60 mL) contained in a 250-mL Erlenmeyer flask. After 10 min, sodium borohydride (0.25 g, 7 mmol) was added to the dark brown solution resulting in a color change to yellow. The product was precipitated by addition of water, collected, and dried. Recrystallization from ethanol gave benzyl diselenide (3.1 g, 80%, mp 91–92 °C).

Method II. Gray powdered selenium (4.74 g, 60 mmol) and sodium borohydride (2.67 g, 70.6 mmol) were placed into a 500 mL, three-necked flask fitted with a nitrogen inlet, addition funnel, and reflux condenser. The flask was flushed with nitrogen, immersed in an ice bath, and absolute ethanol (100 mL) was added slowly with stirring. Stirring was continued until all selenium had dissolved and a colorless solution resulted. To this solution was added morpholine hydrochloride (6.2 g, 50 mmol) followed by benzaldehyde (5.0 g, 47 mmol). The reaction mixture was heated under reflux for 1 h and cooled to room temperature giving a brown solution. Addition of sodium borohydride (0.45 g, 12 mmol) in small doses resulted in a vigorous reaction and change of the solution color from brown to yellow-orange. Addition of water precipitated a yellow product, which was collected by filtration, washed rapidly with a large volume of water (to prevent formation of contaminants from air oxidation of the mother liquor), and dried yielding 6.9 g (86%) of benzyl diselenide. Recrystallized from ethanol the product had mp 92–93 °C, identical with that of an authentic sample. Table II summarizes benzyl diselenide yields obtained by this method with cited variations in reaction conditions. Results with different amines using the above procedure are listed in Table III.

Method III. d. Sodium hydrogen selenide solution was prepared using sodium borohydride (1.89 g, 50 mmol) and gray selenium (4.26 g, 54 mmol) in 100 mL of absolute ethanol as outlined in method II. To this was added morpholine hydrochloride (6.23 g, 50.4 mmol) and benzaldehyde (5.0 g, 47 mmol). This mixture was heated under reflux for 1 h and cooled to room temperature. Addition of water gave a yellow-green precipitate which was collected, washed with water, and dried. This product was extracted with hot methylene chloride, filtered, and solvent was removed in vacuo leaving a yellow solid. Recrystallization from ethanol gave 4.35 g (54%) of benzyl diselenide.

e. To an ethanolic sodium hydrogen selenide solution, made as described above, was added morpholine (4.34 g, 50 mmol) followed by benzaldehyde (5.0 g, 47 mmol) and reaction was continued as described. After cooling, hydrogen chloride (4.2 mL, 50 mmol) was added and the solution was stirred for 60 min at room temperature. Addition of water gave a yellow-green precipitate, which after workup gave benzyl diselenide (4.40 g, 55%).

f. Sodium hydrogen selenide was prepared using gray selenium (3.95 g, 50 mmol) and sodium borohydride (2.08 g, 55 mmol) to which was added 4,4'-benzylideneoimorpholine[19] (12.33 g, 47 mmol). The reaction was continued as described above. Upon cooling, hydrogen chloride was added (8.5 mL, 100 mmol) which after the usual workup gave 4.45 g (56%) of benzyl diselenide.

g. To an ethanolic sodium hydrogen selenide solution containing selenium (5.57 g, 70.5 mmol) and sodium borohydride (2.94 g, 77.6 mmol) was added 12.33 g (47 mmol) of 4,4'-benzylidenedimorpholine. Following the procedure described previously the reaction gave benzyl diselenide (6.5 g, 82%).

Dibenzyl-α,α'-d_2 Diselenide. To NaDSe solution, prepared with Se (2.0 g, 25.5 mmol), $NaBD_4$ (1.07 g 25.5 mmol), and 50 mL of anhydrous ethanol-d_1 was added 1.74 g (20 mmol) of morpholine, 1.68 mL of 38% DCl/D_2O (20 mmol) and 2.12 g (20 mmol) of benzaldehyde. The reaction mixture was heated to reflux for 1 h. After cooling to room temperature, 0.42 g (10 mmol) of $NaBD_4$ was slowly added to the brown mixture resulting in an orange-yellow solution after 15 min. Addition of water precipitated a yellow solid which was thoroughly washed with water and dried in a vacuum desiccator to give dibenzyl-α,α'-d_2 diselenide (1.85 g, 54%). Recrystallization from ethanol gave yellow needles, mp 91–92 °C: NMR ($CDCl_3$) δ 3.70 (1 H, s), δ 7.20 (5 H, s); IR C–D (ν) 2211 cm^{-1} (calcd 2178 cm^{-1}).

Bis(1-naphthylmethyl) Diselenide. 1-Naphthaldehyde (7.3 g, 47 mmol) was reacted with ethanolic sodium hydrogen selenide and morpholine hydrochloride as described in method II. The yellow product was isolated and dried to give 9.4 g (91%) of bis(1-naphthylmethyl) diselenide. Recrystallization from ethanol gave yellow crystalline plates, mp 110–111 °C: NMR ($CDCl_3$) δ 4.15 (s, 2, $-CH_2-$), 7–8.1 (m, 7, $C_{10}H_7$). Anal. Calcd for $C_{22}H_{18}Se_2$: C, 60.01; H, 4.12; Se, 35.87. Found: C, 60.02; H, 4.10; Se, 35.86.

Bis(2-naphthylmethyl) Diselenide. 2-Naphthaldehyde (7.34 g, 47 mmol) was reacted with morpholine hydrochloride and sodium

hydrogen selenide to give 9.5 g (92%) of 2-naphthylmethyl diselenide. Recrystallization from ethanol gave yellow needles, mp 134–135.5 °C: NMR ($CDCl_3$) δ 3.9 (s, 2, $-CH_2Se$), 7–7.8 (m, 7, $C_{10}H_7$). Anal. Calcd for $C_{22}H_{18}Se_2$: C, 60.01; H, 4.12; Se, 35.87. Found: C, 59.89; H, 4.16; Se, 35.83.

Bis(9-anthrylmethyl) Diselenide. 9-Anthraldehyde (9.69 g, 47 mmol) was reacted in a similar fashion with morpholine hydrochloride and sodium hydrogen selenide to yield 11.9 g (90%) of 9-anthrylmethyl diselenide as a yellow crystalline solid upon recrystallization from toluene, mp 193–195 °C (dec). Anal. Calcd for $C_{30}H_{22}Se_2$: C, 66.68; H, 4.10; Se, 29.22. Found: C, 66.65; H, 4.08; Se, 29.25.

Bis(1-dodecyl) Diselenide. Dodecylaldehyde (8.66 g, 47 mmol) was reacted with morpholine HCl and NaHSe as described in method II. After reduction, the resulting product was extracted with CH_2Cl_2 and dried over Na_2SO_4. The solvent was removed in vacuo and the yellow oily residue crystallized from cold ethanol to give 8.5 g (73%) of dodecyl diselenide. Recrystallization from acetone yielded a yellow solid, mp 29.5–30.5 °C (lit.[28] mp 30.5–31 °C): NMR ($CDCl_3$) δ 0.9 (t, 3, CH_3–), 1.3 (s, 20, $-CH_2-$), 3.0 (t, 2, $-CH_2$–Se). IR spectra showed no bands other than those for the alkyl groups in the region 4000–625 cm^{-1}.

Bis(4,4′-*N*,*N*-diethylaminobenzyl) Diselenide. *p*-Diethylaminobenzaldehyde (9.33 g, 47 mmol) was reacted with morpholine hydrochloride, sodium hydrogen selenide, and additional sodium borohydride in the manner described previously. The reaction mixture was extracted with chloroform, washed with water, and dried over $MgSO_4$. Evaporation of solvent in vacuo gave a yellow oil. Dissolved in acetone, the oil was acidified with 5% HCl/EtOH solution to precipitate the *p*-diethylaminobenzyl diselenide·2HCl (8.67 g, 67%) as a yellow crystalline salt, mp 200–202 °C (dec): NMR ($CDCl_2$) δ 1.2 (t, 6, $-CH_3$), 3.6 (b, 4, $-CH_2$–N–), 3.9 (s, 2, $-CH_2$–Se–), 7.2–7.9 (m, 4, Ar). Anal. Calcd for $C_{22}H_{34}N_2Cl_2Se_2$: C, 47.58; H, 6.17; N, 5.04; Cl, 12.77; Se, 28.44. Found: C, 47.33; H, 6.37; N, 4.89; Cl, 12.74; Se, 28.37.

Bis(*p*-methylbenzyl) Diselenide. *p*-Tolualdehyde (6.0 g, 50 mmol) was combined with 4.3 g (50.4 mmol) of piperidine in 70 mL of absolute ethanol and hydrogen selenide as described by method I. Approximately 0.60 g of $NaBH_4$ (13.2 mmol) was added to this solution giving a orange-yellow reaction mixture. The resulting yellow product was recrystallized from methanol and gave yellow needles, 7.8 g (85%) of *p*-methylbenzyl diselenide, mp 61–62 °C: NMR ($CDCl_3$) δ 2.3 (s, 3, CH_3–), 3.73 (s, 2, $-CH_2$Se–), 7.04 (s, 4, Ar). Anal. Calcd for $C_{16}H_{18}Se_2$: C, 52.19; H, 4.93; Se, 42.88. Found: C, 52.18; H, 5.01; Se, 42.82.

Registry No.—Benzaldehyde, 100-52-7; benzyl diselenide, 1482-82-2; *N*,*N*′-benzylidenedipiperidine, 2538-76-3; 4,4′-benzylidenedimorpholine, 6425-08-7; dibenzyl-α,α′-d_2 diselenide, 65915-28-8; bis(1-naphthylmethyl) diselenide, 53391-04-1; 1-naphthaldehyde, 66-77-3; bis(2-naphthylmethyl) diselenide, 53391-03-0; 2-naphthaldehyde, 66-99-9; bis(9-anthrylmethyl) diselenide, 61098-92-8; 9-anthraldehyde, 642-31-9; bis(1-dodecyl) diselenide, 10564-87-1; dodecylaldehyde, 112-54-9; bis(4,4′-*N*,*N*-diethylaminobenzyl) diselenide·2HCl, 65915-29-9; *p*-diethylaminobenzaldehyde, 120-21-8; bis(*p*-methylbenzyl) diselenide, 65915-30-2; *p*-tolualdehyde, 104-87-0; H_2Se, 7783-07-5; NaHSe, 12195-50-5; NaDSe, 12175-25-6.

References and Notes

(1) D. L. Klayman and W. H. H. Günther, "Organic Selenium Compounds: Their Chemistry and Biology", Wiley-Interscience, New York, N.Y., 1973, p 87.
(2) D. S. Margolis and R. W. Pittman, *J. Chem. Soc.*, 799 (1957).
(3) L. B. Agenäs. *Acta. Univ. Ups. Abstr. Uppsala Diss. Sci.*, **132**, 12 (1969).
(4) C. Engler, *Ber.*, **11**, 930 (1878).
(5) E. Baumann and E. Fromm, *Ber.*, **28**, 907 (1895).
(6) L. Mutting, R. M. Silverstein, and C. M. Himel, U.S. Patent 2 951 848 (1961); *Chem. Abstr.*, **55**, 4542*b* (1961).
(7) L. Mutting, R. M. Silverstein, and C. M. Himel, U.S. Patent 3 033 875 (1962); *Chem. Abstr.*, **57**, 124, 380 (1962).
(8) W. H. H. Günther, *J. Org. Chem.*, **32**, 3929 (1967).
(9) V. C. Cohen, *J. Org. Chem.*, **42**, 2510 (1977).
(10) J. W. Lewicki, W. H. H. Günther, and J. Y. C. Chu, *J. Chem. Soc., Chem. Commun.*, 552 (1976).
(11) Beilstein, **20**, -II, 26.
(12) W. H. H. Günther and H. G. Mautner, *J. Med. Chem.*, **7**, 229 (1964).
(13) B. Sjöberg and S. Herdevall, *Acta Chem. Scand.*, **12**, 1347 (1958).
(14) Reference 1, p 36.
(15) D. L. Klayman and T. S. Griffin, *J. Am. Chem. Soc.*, **95**, 197 (1973).
(16) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", McGraw-Hill, New York, N.Y., 1968, p 668.
(17) See ref 16, pp 667–668.
(18) T. S. Woods and D. L. Klayman, *J. Org. Chem.*, **39**, 3716 (1974).
(19) M. Zief and J. P. Mason, *J. Org. Chem.*, **8**, 1 (1943).
(20) M. Renson and R. Collienne, *Bull. Soc. Chim. Belges*, **73**, 491 (1974).
(21) L. Vanino and A. Schinner, *J. Pract. Chem.*, **91**, 116 (1915).
(22) Q. Mingoia, *Gazz. Chim. Ital.*, **58**, 667 (1928).
(23) T. G. Back, D. H. R. Barton, M. R. Britten-Kelly, and F. S. Guziec, Jr., *J. Chem. Soc., Chem. Commun.*, 539 (1975).
(24) Reference 1, p 246.
(25) Reference 1, p 41.
(26) J. Gosselck, H. Barth, and L. Beress, *Justus Liebigs Ann. Chem.*, **671**, 1 (1964).
(27) H. G. Mautner, S. H. Chu, and W. H. H. Günther, *J. Am. Chem. Soc.*, **85**, 3458 (1963).
(28) E. Rebane, *Ark. Kemi*, **25**, 363 (1966).

Iodonium Ylides. The Action of Thiols on Phenyl Dimedonyl Iodone. Oxidation–Reduction vs. Substitution

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The reactions of phenyl dimedonyl iodone (**1**) with various thiophenols, methanethiol, and hydrogen sulfide were studied. With thiophenol, the major process is oxidation–reduction to diphenyl disulfide (**6**) (73%), dimedone (**7**) (70%), and iodobenzene (99%). A 15% yield of phenyl 2-dimedonyl sulfide (**8**), a product of "substitution", was also obtained. The oxidation of thiophenol by **1** apparently proceeds by initial protonation of the latter by the former and subsequent electron transfer from the resulting thiophenoxide ion to the conjugate acid of **1**. The general reaction does not change with para-substituted thiophenols. However, the *ratio* of substitution/oxidation is dependent on the electron-donating capacity of the substituent. With methanethiol the gross reaction is the same. The action of hydrogen sulfide on **1** was reinvestigated, and the spirosulfide **2** (41%), dimedone (**7**) (28%), and 2,2′-bis(dimedonyl) sulfide (**29**) (12%) were obtained.

Introduction

Phenyl dimedonyl iodone (**1**), a stable iodonium ylide,[1] reacts with either phenyl isothiocyanate or methyl isothiocyanate to give low yields of the spirosulfide **2**.[2] Since 5,5-dimethylcyclohexane-1,2-thio,3-trione (**3**) is a possible precursor to **2**, we attempted to prepare authentic **3** by the treatment of **1** with hydrogen sulfide.[2] The thiotrione was not obtained, but the spirosulfide was isolated in 40% yield. We subsequently became interested in the reactions of other sulfhydryl compounds, specifically methanethiol and various thiophenols, with phenyl dimedonyl iodone and now report

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