

than the 1-homoadamantyl cation(11). Further, the cmr spectrum of ion 1 clearly consists of eight lines. The presence of even low concentrations of 1-homoadamantyl cation should immediately complicate the Fourier-transform cmr spectrum of ion 1. This was not found to be the case.

One might also have expected that some methyladamantyl derivatives would also be found in the system. Yet we do not find evidence for the presence of any methyladamantyl derivatives in the quenching experiments.

Taken altogether, the evidence presented clearly indicates the classical, carbenium ion nature of the 3-homoadamantyl cation, and that a cage effect is not important in this case. Determination of the exact geometry of the cation will necessitate further experimental work (including X-ray study). "Cage effects" have been suggested as important factors responsible for the deshielding effect of bridgehead carbon and proton nmr shifts in 1-adamantyl<sup>7</sup> and 1-bicyclo[3.2.2]nonyl<sup>8</sup> cations. The insignificance of such an effect in the distorted 3-homoadamantyl cation (1) seems to indicate that suitable geometry is the primary requirement for such effects.

### Experimental Section

1-Adamantylcarbonyl chloride (9) and 3-homoadamantanol (10) were prepared according to literature procedures.<sup>3b,c</sup>

Quenching of solutions of 3-homoadamantyl cation were carried out in KOH-ice/SO<sub>2</sub>ClF by the previously described procedure.<sup>14</sup>

Preparation of the 3-Homoadamantyl Cation (1). FSO<sub>3</sub>H-SbF<sub>5</sub> (1:1) or a saturated solution of SbF<sub>5</sub> in SO<sub>2</sub>ClF (SO<sub>2</sub>) was prepared and cooled to Dry Ice-acetone bath temperature, ca. -78°. To the solution was then slowly added with vigorous stirring a cold solution of 9 or 10 in SO<sub>2</sub>ClF (SO<sub>2</sub>) to give an approximately 15-20% solution of the ion, which was then transferred to a precooled nmr tube.

Nuclear Magnetic Resonance Spectra. Proton nuclear magnetic resonance spectra (60 MHz and 100 MHz) were obtained by using a Varian Associates Model A56/60A and HA100 nmr spectrometer, respectively. External TMS (capillary tube) was used as reference. Carbon-13 nuclear magnetic resonance spectra were obtained by the fast Fourier-transform method, using Varian HA-100 nmr spectrometer equipped with a variable-temperature probe. Either external methyl iodide or carbon disulfide was used as reference. Carbon chemical shifts were obtained with respect to the external methyl iodide as reference and converted to the carbon disulfide standard. A value of 208.7 ppm was used for  $\delta_{13\text{CH}_3\text{I}}$  (SO<sub>2</sub>ClF, -60°). Off-resonance decoupled cmr spectra<sup>13</sup> were obtained with a coherent radiofrequency, using external CS<sub>2</sub> as reference.

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## Reaction of Selenium with Sodium Borohydride in Protic Solvents. A Facile Method for the Introduction of Selenium into Organic Molecules

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**Abstract:** Elemental powdered selenium and sodium borohydride react very readily in water or ethanol to give either sodium hydrogen selenide or sodium diselenide, depending on the ratio of the reactants. The sodium hydrogen selenide and sodium diselenide solutions, thus prepared, can be utilized directly in typical nucleophilic displacement reactions.

Alkali metal borohydrides have been combined with the chalcogen elements by direct fusion<sup>1,2</sup> and in aprotic solvents such as ether,<sup>2</sup> dioxane,<sup>3</sup> tetrahydrofuran,<sup>4,5</sup> and diglyme.<sup>4,5</sup> Under the latter conditions, sulfur, selenium, and tellurium were incorporated directly into the borohydride.<sup>4,5</sup> The product of the reaction between selenium and sodium borohydride

was reportedly difficult to isolate and its structure was suggested to be NaBH<sub>2</sub>Se<sub>3</sub>.<sup>5</sup>

We have found that, in protic solvents such as water or ethanol, powdered gray selenium reacts rapidly and exothermically at room temperature with sodium borohydride to produce sodium hydrogen selenide (NaHSe) or sodium diselenide (Na<sub>2</sub>Se<sub>2</sub>), depending on the borohydride to selenium ratio.

### Results and Discussion

**Sodium Hydrogen Selenide.** With a 2:1 molar ratio of borohydride to selenium in water, the reaction proceeded according to eq 1 with hydrogen evolution and

$$4\text{NaBH}_4 + 2\text{Se} + 7\text{H}_2\text{O} \longrightarrow 2\text{NaHSe} + \text{Na}_2\text{B}_4\text{O}_7 + 14\text{H}_2 \quad (1)$$

the formation of sodium hydrogen selenide and sodium

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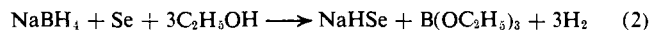
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tetraborate. The pH of a 0.38 M solution, formed as given in eq 1, was 9.0. Thus, it can be calculated from the  $K_1 = 1.3 \times 10^{-4}$  (25°)<sup>6a</sup> and  $K_2 = 10^{-15}$  (22°)<sup>6b</sup> for  $H_2Se$  that the selenium present in such a solution is >99% in the form of hydrogen selenide ions ( $HSe^-$ ) and <0.5% as selenide ions ( $Se^{2-}$ ). The sodium hydrogen selenide was not isolated but was used directly as its aqueous solution in, for example, the preparation of dibenzyl selenide,  $(C_6H_5CH_2)_2Se$ , from benzyl chloride. Thus, it appears that this method for the preparation of dialkyl selenides *via* sodium hydrogen selenide is an alternative to procedures utilizing sodium selenide ( $Na_2Se$ ) produced by the addition of selenium to either sodium in liquid ammonia<sup>7</sup> or to an aqueous solution of alkali and sodium hydroxymethanesulfinate (Rongalite).<sup>8</sup>

Selenium and sodium borohydride were also observed to interact vigorously in methanol and ethanol. The borohydride decomposed very rapidly in methanol, and as a consequence, large excesses were necessary to completely dissolve the selenium. Experiments indicated that the selenium-containing products were triggering the decomposition of the borohydride.

The above was not true, however, in ethanol where the rate of borohydride decomposition was considerably slower. Selenium suspended in ethanol was found to react with sodium borohydride in a 1:1 molar ratio to produce sodium hydrogen selenide and triethyl borate, as shown in eq 2. The method given in eq 2



is very simple and compares favorably with the earlier reported technique for the preparation of ethanolic solutions of sodium hydrogen selenide. The latter involves passing hydrogen selenide gas, usually generated by acid hydrolysis of aluminum selenide, into a solution of sodium ethoxide in ethanol.<sup>9</sup> The ethanolic solution of sodium hydrogen selenide is advantageous in that it provides a superior solvent for nucleophilic displacement reactions on water-insoluble or hydrolysis-sensitive organic compounds. The sodium hydrogen selenide solution, prepared by the borohydride reduction, can be used directly in various displacement reactions since the by-product, triethyl borate, will not interfere. In subsequent work-up of the selenium-containing product, the triethyl borate can be removed by evaporation [bp 118° (743 mm)]<sup>10</sup> or by hydrolysis to boric acid and ethanol. In typical utilizations, sodium hydrogen selenide reacted with benzyl chloride to give benzylselenol ( $C_6H_5CH_2SeH$ ) in satisfactory yield. An attempt to make benzylselenol by the reaction of benzyl chloride with aqueous sodium hydrogen selenide, produced as shown in eq 1, resulted in the formation of dibenzyl selenide exclusively. Also 1,1-diphenyl-2-selenourea was prepared in 89% yield by the reaction of 1,1-diphenyl-2-methyl-2-thiopseudourea hydriodide with

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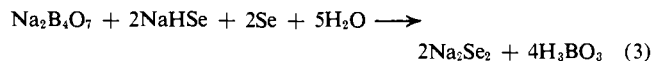
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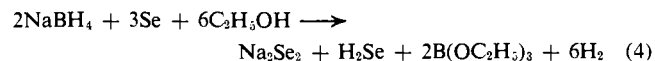
ethanolic sodium hydrogen selenide. The selenourea was prepared earlier<sup>11</sup> by this procedure utilizing an aqueous-ethanolic sodium hydrogen selenide solution which had been produced from gaseous hydrogen selenide.

**Sodium Diselenide.** By adding 1 equiv of selenium to the aqueous sodium hydrogen selenide solution, produced as described earlier, it was possible to generate the characteristic brownish red solution of sodium diselenide (eq 3). The by-product of the reaction was

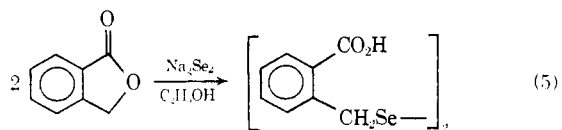


boric acid. About 15 min of warming on the steam bath was required to complete the dissolution of the selenium in the hydrogen selenide solution. The aqueous sodium diselenide and benzyl chloride on reaction gave dibenzyl diselenide,  $(C_6H_5CH_2Se)_2$ , in 77% yield.

The methods available for the preparation of alcoholic solutions of sodium diselenide include the reaction of selenium with ethanolic sodium hydrogen selenide generated, as previously mentioned, from hydrogen selenide and sodium ethoxide.<sup>12</sup> In addition, the formation of bis(methoxymagnesium) diselenide provides diselenide ions in methanol.<sup>13</sup> Therefore, it was of interest to observe that a solution of sodium diselenide in ethanol could be simply prepared by using a 2:3 molar ratio of sodium borohydride to selenium as indicated in eq 4. The reaction mixture was heated for 1.5



hr under reflux while nitrogen passed through the mixture. The expulsion of hydrogen selenide helped drive the reaction to completion. The resultant brownish red solution, on heating with benzyl chloride, gave dibenzyl diselenide in 92% yield. Although this yield was higher than that produced in water, the aqueous sodium diselenide (eq 3) is probably the reagent of choice for the preparation of simple diselenides since it is not necessary to expel hydrogen selenide. For the reaction of sodium diselenide with substrates that require elevated temperatures, however, the ethanolic solution (eq 4) is preferable, if not mandatory, since at higher temperatures, the aqueous solution steadily evolves hydrogen selenide. For example, phthalide was ring-opened with sodium diselenide in ethanol (reflux 40 hr) to form bis(2-carboxybenzyl) diselenide<sup>13</sup> in 86% yield, whereas the same reaction performed in water (reflux 40 hr) produced only a 30% yield of the diselenide (eq 5) and a 54% loss of selenium in the form of hydrogen selenide.



**Reaction of Sodium Borohydride with Sulfur and Tellurium.** In contrast to the behavior of selenium, powdered sulfur was essentially inert to the action of

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sodium borohydride in water at room temperature. It reacted vigorously, however, in ethanol to form sodium hydrogen sulfide in a reaction analogous to that depicted in eq 2. Tellurium reacted very slowly in water with sodium borohydride to form what is presumed to be a solution of sodium hydrogen telluride, but was unreactive in ethanol.

### Experimental Section

Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Microanalyses were performed by Mr. Joseph F. Alicino, New Hope, Pa. 18938. Infrared spectra were determined on a Beckman IR-5 spectrophotometer. Nmr spectra were taken on a Varian A-60 using TMS as an internal standard. Mass spectral analyses were performed on a Varian EM-600 mass spectrometer at 70 eV.

All the reactions were run under a nitrogen atmosphere to prevent oxidation of the oxygen-sensitive selenide ions and selenium-containing products. Selenium was used in its gray powdered form.

**Sodium Hydrogen Selenide (Aqueous).** Sodium borohydride (2.3 g, 61 mmol) in 25 ml of water was added with magnetic stirring at room temperature to 2.3 g (29 mmol) of selenium suspended in 25 ml of water. Considerable foaming ( $H_2$ ) occurred immediately in the vigorous reaction and the selenium was consumed in less than 5 min. The virtually colorless solution of NaHSe which resulted was ready for use without further treatment.

Upon cooling of the solution, 4.0 g of crystals separated whose ir spectrum (KBr) was identical with the published<sup>14</sup> spectrum of  $Na_2B_3O_7 \cdot 10H_2O$ .

**Dibenzyl Selenide.** To an aqueous solution of sodium hydrogen selenide, prepared as described above, was added 7.3 g (58 mmol) of benzyl chloride, and the mixture was stirred at room temperature for ca. 17 hr. The solid product was collected, washed with water, and recrystallized from pentane. The dibenzyl selenide, 6.5 g (86%), crystallized as pale yellow rods, mp 44–45° (lit.<sup>15</sup> mp 45.5°), ir (KBr) identical with that of an authentic sample.

**Sodium Hydrogen Selenide (Ethanol).** Absolute ethanol (150 ml) was added with magnetic stirring to 6.0 g (76 mmol) of selenium and 3.2 g (84 mmol) of sodium borohydride cooled in an ice bath. After the initial vigorous foaming had subsided (15 min), the ice bath was removed and the nearly colorless ethanolic solution of NaHSe was ready for further use.

Partial removal of the solvent and distillation afforded triethyl borate,  $B(OC_2H_5)_3$ , bp 105–110° (763 mm) [lit.<sup>10</sup> bp 118° (743 mm)], mass spectrum  $m/e$  146 ( $M^+$ ); the ir spectrum ( $CHCl_3$ ) was identical with the known spectrum.<sup>16</sup>

**Benzylselenol.** Benzyl chloride (9.7 g, 76 mmol) was added with stirring to an ethanolic solution of sodium hydrogen selenide, prepared as described above, and the reaction was allowed to stand at room temperature for ca. 5 hr. Deoxygenated water (200 ml) was added with sufficient dilute hydrochloric acid to lower the pH to 5–6. Nitrogen was bubbled through the mixture for about 45 min to remove  $H_2Se$  (caution)<sup>17</sup> and the product was extracted into  $CHCl_3$ . The  $CHCl_3$  was then removed *in vacuo* leaving a gray oil which was found to be about 65% benzylselenol and 35% dibenzyl selenide by nmr. The benzylselenol was separated from the latter compound by distillation [bp 82° (10 mm); lit.<sup>18</sup> bp 101–102° (2 mm)] yielding 6.6 g (51%) of a colorless oil; ir (neat) 4.35  $\mu$  (SeH), lit.<sup>19</sup> 4.35  $\mu$ ; nmr ( $CDCl_3$ )  $\delta$  -0.09 (t, 1,  $J$  = 6.5 Hz, SeH), 3.64 (d, 2,  $J$  = 6.5 Hz,  $-CH_2-$ ), 7.17 (s, 5,  $C_6H_5$ ).

**1,1-Diphenyl-2-selenourea.** Absolute ethanol (50 ml) was added with magnetic stirring to 1.0 g (27 mmol) of sodium borohydride and 2.0 g (25 mmol) of selenium cooled in an ice bath, as outlined above. 1,1-Diphenyl-2-methyl-2-thiopseudourea hydriodide (5.0 g, 14 mmol) in 25 ml of ethanol was added with stirring and the solution was allowed to stand for ca. 15 hr at room temperature. Glacial

acetic acid was added to adjust the pH to 5–6 while  $N_2$  bubbled through the solution for 30 min to expel  $H_2Se$ .<sup>17</sup> The solvent was removed *in vacuo* and the residue was extracted with  $CHCl_3$ . Evaporation of the  $CHCl_3$  and recrystallization of the residue from  $CHCl_3$ -hexane yielded 3.3 g (89%) of 1,1-diphenyl-2-selenourea, mp 200° dec (lit.<sup>11</sup> mp 205–207° dec); the ir spectrum (KBr) was identical with that of an authentic sample.

**Sodium Diselenide (Aqueous).** Sodium borohydride (3.0 g, 79 mmol) in 25 ml of water was added with magnetic stirring to 3.0 g (38 mmol) of selenium suspended in 25 ml of water at room temperature. After the initial vigorous reaction had subsided (10 min), 1 additional equiv of selenium (3.0 g, 38 mmol) was added. The mixture was stirred for 15 min and then warmed briefly on the steam bath to complete the dissolution of the selenium. The brownish red aqueous solution of  $Na_2Se_2$  was then ready for further use.

**Dibenzyl Diselenide.** Benzyl chloride (9.6 g, 76 mmol) was added with magnetic stirring to an aqueous sodium diselenide solution prepared as described above, and the mixture was stirred for ca. 19 hr at room temperature. The yellow solid was collected, washed with water, and recrystallized from ethyl acetate-hexane yielding 9.9 g (77%) of dibenzyl diselenide, mp 92–94° (lit.<sup>20</sup> mp 92–93°); the ir spectrum (KBr) was identical with that of an authentic sample.

When the aqueous filtrate was cooled, 1.7 g of  $H_3BO_3$  was collected; the ir spectrum (KBr) was identical with the published spectrum.<sup>14</sup>

**Sodium Diselenide (Ethanolic).** Absolute ethanol (150 ml) was added with magnetic stirring to 3.0 g (38 mmol) of selenium and 1.0 g (27 mmol) of sodium borohydride cooled in an ice bath. After the initial reaction had subsided, the mixture was stirred and heated at reflux for 1.5 hr with  $N_2$  passing into the liquid in order to dissolve the selenium and expel  $H_2Se$  (caution).<sup>17</sup> The brownish red ethanolic solution of  $Na_2Se_2$  was then ready for further use.

**Dibenzyl Diselenide.** To an ethanolic sodium diselenide solution, made as described above, was added 3.2 g (25 mmol) of benzyl chloride, and the solution was heated at reflux for 4 hr. After cooling and acidification with glacial acetic acid,  $N_2$  was passed through the mixture for 15 min to remove any  $H_2Se$ .<sup>17</sup> The solvents were removed *in vacuo* and the residue was extracted with hot  $CHCl_3$ . Evaporation of the  $CHCl_3$  gave the product which was recrystallized from hexane yielding 4.0 g (92%) of dibenzyl diselenide, mp 87–89° (lit.<sup>21</sup> mp 92–93°); the ir spectrum (KBr) was identical with that of an authentic sample.

**Phthalide Ring Opening. In Ethanol.** Absolute ethanol (65 ml) was added with magnetic stirring to 2.0 g (25 mmol) of selenium and 0.7 g (18 mmol) of sodium borohydride as outlined above. The mixture was stirred and heated at reflux for 1.5 hr with  $N_2$  passing into the liquid.<sup>17</sup> Phthalide (2.3 g, 17 mmol) was added and the mixture was stirred and heated under reflux for 40 hr. The cooled mixture was acidified with dilute hydrochloric acid and briefly purged with  $N_2$  to expel any  $H_2Se$ .<sup>17</sup> The tan-colored material was collected and dissolved in dilute NaOH, and the solution was aerated for 15 min. The red selenium which precipitated was removed and the filtrate was acidified to yield 3.12 g (86%) of bis-(2-carboxybenzyl) diselenide, mp 217–218° (lit.<sup>13</sup> mp 215–218°); ir (KBr) 3.45 and 5.95  $\mu$  (COOH). The melting point was not changed on recrystallization from ethanol.

*Anal.* Calcd for  $C_{18}H_{14}O_4Se_2$ : C, 44.88; H, 3.30; Se, 36.88. Found: C, 44.49; H, 3.02; Se, 37.57.

**In Water.** To 150 ml of an aqueous solution of  $Na_2Se_2$ , prepared from 3.0 g (38 mmol) of selenium and 1.5 g (40 mmol) of sodium borohydride, was added 5.8 g (40 mmol) of phthalide, and the mixture was stirred and heated under reflux for 40 hr. The slow evolution of  $H_2Se$  was detected throughout the course of the reaction.<sup>11</sup> After cooling, the yellow mixture was extracted with  $CHCl_3$ . Then the aqueous layer was acidified with dilute hydrochloric acid and the precipitate was collected and washed with water, yielding 2.4 g of bis-(2-carboxybenzyl) diselenide. From the  $CHCl_3$  layer was recovered 1.8 g of phthalide. The lead selenide (5.9 g) from the lead acetate trap corresponds to a 54% loss of selenium as  $H_2Se$ .

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