Some New 3-Substituted 3-Hydroxyselenetanes and Their Loss of Selenium[1]

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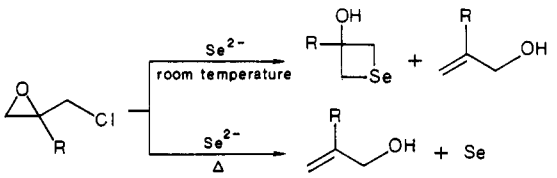
3-Phenyl-, 3-(*p*-methoxyphenyl)-, and 3-ethyl-3-hydroxyselenetane were prepared by treatment of 2-substituted 2-(chloromethyl)oxiranes with selenide ion at room temperature or lower. At elevated temperatures 2-substituted allyl alcohols were the major products. Treatment of 3-phenyl-3-hydroxyselenetane with base gave 2-phenyl-2-propenol, and attempts to prepare the benzoate and 3,5-dinitrobenzoate of 3-phenyl-3-hydroxyselenetane resulted in the formation of the benzoates of 2-phenyl-2-propenol. The acetate and 3,5-dinitrobenzoate of 3-hydroxyselenetane could be prepared, but they decompose on attempted purification. NMR evidence is obtained for the formation of 3-selenetanone by oxidation of 3-hydroxyselenetane with the Dess–Martin periodinane. An explanation is advanced for the differences in behavior of sulfide, selenide, and telluride ion toward (chloromethyl)oxiranes. An attempt to prepare 3-hydroxytelluretane from 1,3-dibromo-2-propanol and telluride ion gave only isopropyl alcohol.

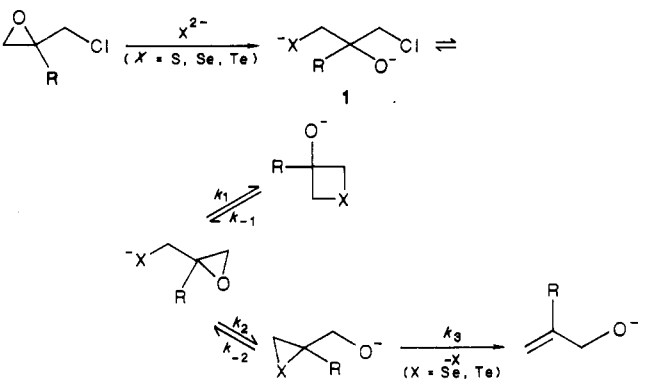
Four-membered selenium heterocycles with one selenium atom are relatively rare, examples being limited to selenetane itself,[2] four 3,3-disubstituted selenetanes[3-6] including two spiro derivatives,[5] and 3-hydroxyselenetane.[7] A few selenuranes,[3] which contain a tetravalent selenium atom, and other four-membered cyclic selenium-containing compounds with more than one heteroatom are known.[8]

We prepared several new 3-substituted-3-hydroxyselenetanes by treating 2-substituted 2-(chloromethyl)oxiranes with selenide ion at room temperature or lower, a reaction patterned on the reaction of sulfide ion with (chloromethyl)oxiranes (epichlorohydrins)[9] and obviously related to the synthesis of 3-hydroxyselenetane from (chloromethyl)oxirane and selenide ion.[7b-d] At higher temperatures no hydroxyselenetanes were obtained, 2-substituted propenols being the major products. Similar reactions with telluride ion give only the allyl alcohol even at room temperature.[10] Treatment of epichlorohydrins with sulfide ion gives only hydroxythietanes, there being no loss of elemental sulfur.[9]

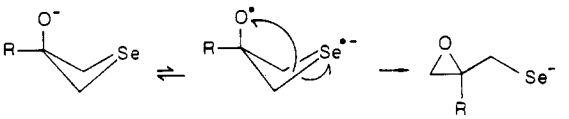


A rationalization (Scheme I) of these differences in reactivity of sulfide, selenide, and telluride ions toward epichlorohydrins under basic conditions depends on assuming an equilibrium between three- and four-membered heterocycles with the proviso that epitellurides lose elemental tellurium rapidly and irreversibly. At lower temperatures episelenides are stable but they lose elemental selenium irreversibly at higher temperatures as reported by Chan and Finkenbine.[11] Episulfides are stable. The reversibility of formation of four-membered selenetanes and telluretanes means that ultimately the allyl alcohol will be formed via the episelenide or epitelluride, whereas with sulfide ion both three- and four-membered rings can be formed with the less-reactive hydroxythietane predominating over the more reactive episulfide ($k_{-2} > k_{-1}$). The four-membered rings may be formed directly from the epichlorohydrin via intermediate **1**, although in general cyclization to three-membered rings is faster than to four-membered rings.[12]

Scheme I



The k_{-1} step in Scheme I is classified as "3-exo-tet" and is stereoelectronically allowed,[13] but the four-membered ring probably places some constraint on the displacement by the alkoxide ion. The difficulty in positioning the oxygen nucleophile for optimum S_N2 geometry is mitigated by long and weak (relative to carbon–sulfur) carbon–tellurium or carbon–selenium bonds so that k_{-1} for these chalcogens is greater than for sulfur. Alternatively, the k_{-1} step may involve a one-electron transfer from alkoxide ion to an empty (e.g., σ^*) orbital involving the chalcogen.



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(2) (a) Morgan, G. T.; Burstall, F. H. *J. Chem. Soc.* **1930**, 1497. (b) Harvey, A. B; Durig, J. R.; Morrissey, A. C. *J. Chem. Phys.* **1969**, *50*, 4949.
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(11) Chan, T.; Finkenbine, J. R. *Tetrahedron Lett.* **1974**, 2091.
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(13) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.

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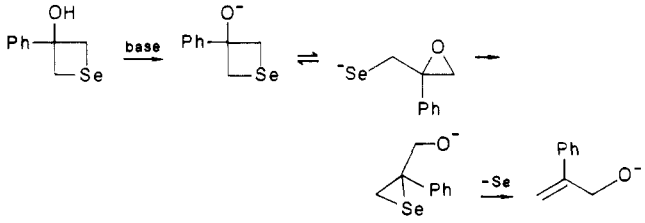
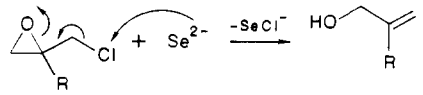
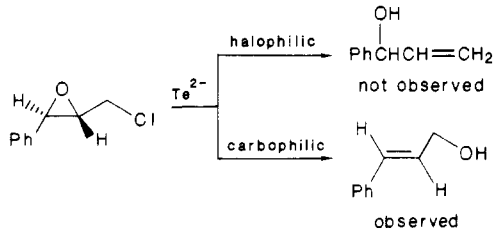
The reversibility of the selenetane-forming reaction was demonstrated when 3-phenyl-3-hydroxyselenetane was treated with base under conditions used in the reaction with telluride ion[10] to give 2-phenyl-2-propenol.



Another mechanism for the formation of allyl alcohols from the (chloromethyl)oxiranes involves halophilic attack by selenide ion:

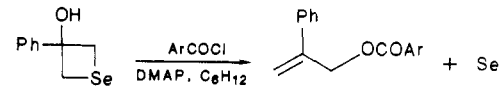


However, treatment of the epoxide of *trans*-cinnamyl chloride with telluride ion gives only the product expected from carbophilic attack.[10] In general, halophilic attack on chlorine is much less favorable than for bromine or iodine.[14] The affinity of hydrogen telluride ion for activated halogens is said not to be shared by hydrogen selenide ion,[15] so that if halophilic attack were to occur on the (chloromethyl)oxirane, telluride ion would be favored over selenide ion. Since telluride ion attacks only carbon, it is likely that selenide ion does also.

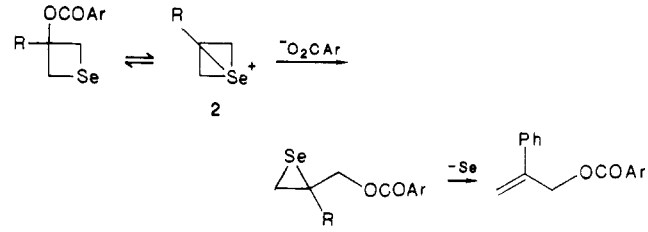


3-Hydroxyselenetene is obtained by treatment of 1,3-dibromo-2-propanol with selenide ion, no reductive dehalogenation being observed,[7a] and phenyl selenide ion attacks the carbon atoms of epichlorohydrin and 1,3-dichloro-2-propanol, as does selenide ion itself.[7b,d] However, we find that 1,3-dibromo-2-propanol is reduced to isopropyl alcohol by telluride ions, apparently by a halophilic attack or a one-electron-transfer mechanism.

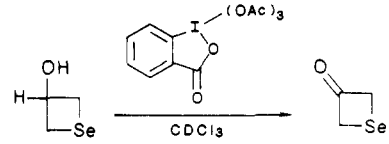
The mass spectra of 3-substituted 3-hydroxyselenetanes are similar to that of 3-hydroxythietane[17] and show ions at m/e 94 corresponding to $CH_2Se^{\bullet+}$. These selenetanes are labile compounds, unstable to heat, and acids. When 3-phenyl-3-hydroxyselenetane is treated with benzoyl or 3,5-dinitrobenzoyl chloride in the presence of 4-(dimethylamino)pyridine (DMAP), the corresponding benzoates of 2-phenyl-2-propenol were obtained. Red elemental selenium deposited from these reaction mixtures. The acetate and 3,5-dinitrobenzoate of unsubstituted 3-hydroxyselenetane can be prepared, but these derivatives decomposed when purification was attempted. Their mass spectra show the loss of the acid (acetic or benzoic) from the molecular ion to give the cation radical of the unknown selenete (selenacyclobutene).



One possible explanation for this behavior with the two acid chlorides is that the selenium atom transannularly displaces a leaving group at the 3-position of the ring, followed by nucleophilic attack on the bicyclic episelenonium ion **2**, to yield an episelenide which loses elemental selenium. This type of decomposition is noted also with thietanes but to a lesser degree and without extrusion of elemental sulfur.[18]



Evidence for the formation of the previously unknown 3-ketoselenetane is the change in appearance of the ^1H NMR spectrum when 3-hydroxyselenetane is treated with the Dess–Martin periodinane, a reagent recommended for selective oxidation of primary and secondary hydroxy groups.[19] The complex AA'BB'X multiplet of the alcohol became a singlet (δ 4.22) as expected for the ketone. The corresponding 3-thietanone,[20] prepared by oxidation of 3-thietanol by the periodinane, shows a singlet at δ 4.21. 3-Ketoselenetane is not stable and could not be isolated, perhaps a consequence of its having an electrophilic group at the 3-position.



Experimental Section

All melting points were taken on a Reichert micro-hot stage and are uncorrected. ^1H NMR spectra were obtained on a Varian T-60 or a 250-MHz Mohawk spectrometer. ^{13}C NMR spectra were obtained on a 500-MHz GE Nicolet spectrometer operating at 125.76 MHz. Infrared spectra were recorded on a Beckman Model 4220 spectrometer, and mass spectra were obtained on a Finnegan Mat 4000 GC/MS instrument. High-resolution mass spectra were obtained at Cornell University, Ithaca, NY. Elemental analyses were done at Galbraith Laboratories, Knoxville, TN. Preparative TLCs were done on EM 5715 60 F 20 × 20 cm. plates. Analytical TLCs were visualized either with iodine, ultraviolet light, or by a molybdic acid spray.

Solvents were distilled prior to use. THF was distilled from sodium and benzophenone ketyl; ethyl ether was distilled over lithium aluminum hydride. 1,3-Dichloro-2-propanone, Grignard reagents, and gray selenium powder were obtained commercially.

General Procedure. The Grignard reagent was added to a solution of 1,3-dichloro-2-propanone in dry THF at −60 °C as previously described.[21] The addition was done over a period of 2 h with vigorous mechanical stirring, and the reaction mixture

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was worked up with aqueous ammonium chloride and extracted with ethyl ether, dried ($MgSO_4$), and evaporated to obtain the tertiary alcohol. The tertiary alcohols were mixed with a slurry of calcium hydroxide in water and ether, and the mixture was refluxed until all the alcohol was consumed. Extraction with ether, drying, and removal of the ether yielded the (chloromethyl)oxiranes.

3-Hydroxyselenetanes. General Procedure. A suspension of lithium selenide was prepared by the method of Gladysz and co-workers[22] from approximately equimolar quantities of lithium triethylborohydride and gray selenium in dry tetrahydrofuran (THF). After evolution of hydrogen had ceased, additional THF (10 mL) was added, and the mixture was stirred under nitrogen for 20 min followed by addition of a few drops of *tert*-butyl alcohol and dry THF (5 mL) to ensure complete consumption of the superhydride. The (chloromethyl)oxirane (approximately equimolar with selenide ion) in dry THF (20 mL) was added via a syringe pump during 10 h. The solution of selenide ion was cooled (0 °C) for the addition of the *p*-methoxyphenyl derivative; for the other oxiranes the selenide solution was at room temperature. The milky slurry became a red solution. Distilled water (20 mL) was added, and the mixture was extracted with ether. The ether extracts were passed through a column of silica gel under nitrogen pressure to remove lithium chloride. The red solution was dried and evaporated to give a dark red oil, which was purified by preparative TLC (3:7 ether–petroleum ether). The selenetanes are pale yellow liquids with little or no odor. They turn red on long standing. The 3-substituted hydroxyselenetanes decompose on attempted purified by distillation.

3-Hydroxyselenetane: bp 60–62 °C (0.8 mm) (lit.[7a] bp 80–85 °C (3.5 mm)); yield 75%; ^1H NMR ($CDCl_3$) δ 3.12–3.37 (dt, 4 H, J = 8 Hz) 4.20 (br s, 1 H), 4.85 (m, 1 H, J = 8 Hz); ^{13}C NMR ($CDCl_3$) δ 27.9, 68.1; IR (neat) 3600–3100 (vs, br), 1160 (s), 1118 (s) cm^{-1}; MS (70 eV), m/e (relative intensity) 140 (5), 138 (60, M), 136 (26), 135 (5), 134 (6), 96 (13), 94 (100, CH_2Se), 92 (45), 91 (22), 90 (15), 57 (21), 44 (30, C_2H_4O), 43 (84), 42 (11), 39 (42). This selenetane also was prepared in 56% yield by treatment of 1,3-dibromopropanol with sodium hydrogen selenide[23] in water–methylene chloride in the presence of a phase-transfer catalyst (cetyltrimethylammonium bromide).

Reaction of 1,3-Dibromo-2-propanol with Telluride Ion. 1,3-Dibromo-2-propanol (5.0 g, 23 mmol) was added dropwise over a period of 10 h to a purple solution of sodium telluride prepared according to the Tschugaeff method.[24] Stirring was continued over an additional 2 h at 50 °C. The solution was filtered through Celite to remove precipitated tellurium and resinous material and the filtrate extracted with chloroform (8 × 25 mL). The solvent was removed by rotary evaporation to give 2-propanol (0.22 g; 4.7 mmol, 20%): ^1H NMR (60 MHz, $CDCl_3$) δ 1.25 (d, 6 H, CH_3), 2.25 (br s, 1 H, OH), 3.71 (m, 1 H, CH) [identical with the ^1H NMR spectrum of an authentic sample]. Gas chromatographic analysis was done on a Varian 3740 4-ft 20% Carbowax 20 M column, and the retention time (0.73 min; temperature program: 50–120 °C at 5 °C/min; injection 200 °C, detection 240 °C) corresponds with that of an authentic sample of 2-propanol (retention time 0.74 min.)

3-Phenyl-3-hydroxyselenetane: yield 55%; ^1H NMR ($CDCl_3$) δ 3.40–3.44 (d, 2 H, J = 9.1 Hz), 3.46–3.50 (d, 2 H, J = 9.1 Hz), 3.73 (s, 1 H), 7.29–7.63 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 30.5, 79.5, 124.1, 127.7, 128.3, 145.0; IR (neat) 3600–3200 (vs, br), 1180 (m), 1140 (m), 1040 (s), 1030 (s), 760 (s), 690 (s) cm^{-1}; MS (70 eV), m/e (relative intensity) 216 (2), 214 (19, M), 212 (9), 211 (2), 210 (3), 120 (55), 105 (100, PhCO), 96 (1), 94 (7), 92 (11), 91 (33), 90 (4), 78 (50), 77 (44), 65 (11), 51 (28), 50 (13), 43 (19) 39 (21); high-resolution mass spectrum, calcd for $C_9H_{10}OSe$ 213.9896, found 213.9913. 2-Phenyl-2-propenol (10%) was a minor product identified by comparison of its ^1H and ^{13}C NMR, infrared, and mass spectra with those of an authentic sample.

3-(*p*-Methoxyphenyl)-3-hydroxyselenetane: yield 66.6%; ^1H NMR ($CDCl_3$) δ 2.92 (s, 1 H), 3.46–3.50 (d, 2 H, J = 9.4 Hz), 3.58–3.61 (d, 2 H, J = 9.4Hz), 3.81 (s, 3 H), 6.91–6.95 (d, 2 H), 7.55–7.59 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 31.0, 55.3, 79.9, 113.9, 125.7, 137.7, 159.3; IR (neat) 3600–3200 (s, br), 1240 (s), 1170 (s), 1020 (s), 820 (s) cm^{-1}; MS (70 eV), m/e (relative intensity) 246 (1), 244 (5, M), 242 (2), 241 (1), 240 (1), 151 (10), 150 (100), 135 (84, $CH_3OC_6H_4CO$), 121 (16), 108 (13), 96 (1), 94 (6), 92 (8), 91 (8), 90 (4), 78 (13), 77 (31), 63 (11), 51 (11), 43 (14), 39 (15); high-resolution mass spectrum, calcd for $C_{10}H_{12}O_2Se$ 244.0002, found 243.9972. 2-(*p*-Methoxyphenyl)-2-propenol[10] (5%) was a minor product identified by its spectra and its high-resolution mass spectrum: calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0833.

3-Ethyl-3-hydroxyselenetane: yield 58%; ^1H NMR ($CDCl_3$) δ 0.95–1.01 (t, 3 H), 1.91–2.01 (q, 2 H), 3.02–3.05 (d, 2 H, J = 9.4 Hz), 3.32–3.36 (d, 2 H, J = 9.4 Hz), 3.38 (s, 1 H); IR (neat) 3600–3200 (s, br), 1190 (m), 1120 (w), 1090 (w), 980 (s) cm^{-1}; MS, (70 eV) m/e (relative intensity) 168 (3), 166 (17, M), 164 (9), 163 (3), 162 (3), 110 (9), 96 (2), 94 (8), 92 (4), 91 (3), 90 (2), 72 (28), 57 (100), 43 (81), 41 (12), 39 (13). Anal. Calcd for $C_5H_{10}OSe$: C, 35.92; H, 6.50; Se, 47.66. Found: C, 36.36; H, 6.10; Se, 47.82.

Reaction of 2-Phenyl- or 2-(*p*-Methoxyphenyl)-2-(chloromethyl)oxirane with Lithium Selenide at 67 °C. The oxirane (0.60 or 0.50 mmol, respectively) was added to the selenide solution via syringe, and the mixture was refluxed 4 h. The solution was stirred at room temperature overnight. Selenium deposited at the bottom of the flask as a fine, red precipitate. The mixture was poured into distilled water (10 mL) and extracted with ether (3 × 10 mL), the ether extracts were dried ($MgSO_4$), and the solvents were removed on a rotary evaporator to give a yellow oil. This was purified by preparative TLC (3:7 ether–hexane) to give 2-phenyl-2-propenol (70%) or 2-(*p*-methoxyphenyl)-2-propenol[10] (48%), mp 71–73 °C, identified by their IR and NMR spectra.

Conversion of 3-Phenyl-3-hydroxyselenetane to 2-Phenyl-2-propenol. 3-Phenyl-3-hydroxyselenetane (0.05 g, 0.24 mmol) in dioxane (5 mL) was added to a warm (55 °C), aqueous solution of sodium formaldehyde sulfoxylate (Rongalite) (0.20 g, 1.30 mmol) and sodium hydroxide (0.16 g, 3.89 mmol), and the mixture was refluxed for 4 h. The red solution was filtered through Celite and extracted with chloroform (3 × 5 mL). The extracts were concentrated and filtered through silica gel. The silica gel was washed with ether. Removal of the ether gave 2-phenyl-2-propenol (0.0078 g; 0.058 mmol, 25%) identified by comparison of its ^1H NMR and IR spectra with those of an authentic sample.[25] Refluxing a small sample of 3-phenyl-3-hydroxyselenetane in pentane–ether with sodium hydride resulted in precipitation of red selenium. TLC (3:7 ether–hexane) indicated the presence of 2-phenyl-2-propenol by comparison of the R_f value with that of an authentic sample.

Reaction of 3-Phenyl-3-hydroxyselenetane with 3,5-Dinitrobenzoyl Chloride and with Benzoyl Chloride. 3-Phenyl-3-hydroxyselenetane (0.04 g, 0.19 mmol) in cyclohexane (5 mL) was added to a mixture of 4-(dimethylamino)pyridine (0.11 g, 0.94 mmol) and 3,5-dinitrobenzoyl chloride (0.24 g, 1.03 mmol) in cyclohexane (5 mL), and the mixture was stirred under nitrogen for 12 h. The mixture was acidified with aqueous hydrochloric acid (5 mL, 10%), and the precipitate of red selenium was removed by filtration through glass wool. The filtrate was washed with ether (5 mL), and the aqueous solution was extracted with ether. The ether extracts were dried and evaporated on a rotary evaporator to give a white solid, which was recrystallized from hot ether to give white needles of the 3,5-dinitrobenzoate of 2-phenyl-2-propenol (0.26 g, 0.80 mmol, 85%): mp 116–118 °C (lit.[25] mp 116–117 °C); ^1H NMR ($CDCl_3$) δ 5.42 (s, 2 H) 5.53 (s, 1 H), 5.71 (s, 1 H), 7.40–7.61 (m, 5 H), 9.10–9.22 (m, 3 H).

A similar reaction of 3-phenyl-3-hydroxyselenetane (0.05 g, 0.23 mmol) with 4-(dimethylamino)pyridine (0.03 g. 0.25 mmol) and benzoyl chloride (0.05 g, 0.36 mmol) in cyclohexane (3 mL) gave the benzoate of 2-phenyl-2-propenol,[25] a clear oil (0.030 g, 0.14 mmol, 59%): ^1H NMR ($CDCl_3$) δ 5.23 (s, 2 H), 5.45 (s, 1 H), 5.61 (s, 1 H), 7.21–8.21 (m, 5 H).

3,5-Dinitrobenzoate of 3-Hydroxyselenetane. 3,5-Dinitrobenzoyl chloride (0.30 g, 130 mmol) was stirred with a solution of 3-hydroxyselenetane (0.15 g, 1.08 mmol) in dry pyridine (2 mL) for 0.5 h. The mixture was carefully poured into ice–water (5 mL)

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(24) Tschugaeff, L.; Chlopin, W. *Chem. Ber.* **1914**, *47*, 1269.
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and acidified with hydrochloric acid (10%, 5 mL). A yellow precipitate of the dinitrobenzoate was removed by filtration and washed with aqueous sodium bicarbonate (10%, 5 mL). Recrystallization from cold carbon tetrachloride gave the 3,5-dinitrobenzoate as an amorphous golden yellow powder (0.29 g, 0.89 mmol, 82%): mp 127–128 °C (dec); ^{1}H NMR ($CDCl_3$) δ 3.27–3.33 (dd, 2 H), 3.67–3.74 (dd, 2 H), 5.96–6.04 (m, 1 H), 9.13–9.25 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 23.3, 70.6, 122.7, 129.4, 133.5, 148.7; IR (KBr) 1740 (vs), 1640 (s), 1550 (vs), 1350 (vs), 1180 (s), 740 (s), 730 (s) cm^{-1}; MS (70 eV), *m/e* (relative intensity) 334 (1), 332 (7, M), 330 (2), 329 (1), 328 (1), 196 (7), 195 (100), 149 (42), 122 (13), 121 (49), 120 (78), 119 (30), 118 (42), 117 (21), 116 (13), 103 (13), 96 (3), 94 (22), 93 (22), 92 (11), 91 (17), 75 (80), 74 (26). Anal. Calcd for $C_{10}H_8O_6N_2Se$: C, 36.27; H, 2.44. Found: C, 35.54; H 2.64. The elemental analysis is not satisfactory due to the instability of the compound.

3-Acetoxyselenetane. 3-Hydroxyselenetane (0.30 g, 2.20 mmol) was mixed with acetic anhydride (2 mL, 2.36 mmol) and sodium acetate (0.28 g, 2.80 m mol) and refluxed gently under a nitrogen atmosphere for 1.5 h. A fine, red precipitate could be seen at the bottom of the flask. The reaction mixture was poured into distilled water (5 mL) and extracted with ether (3 × 20 mL). The ether extracts were dried ($MgSO_4$) and concentrated to give a red-yellow oil. Preparative TLC (silica gel, 3:7 ether–petroleum ether) gave 3-acetoxyselenetane as yellow oil (0.105 g, 0.58 mmol, 27%): ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 3 H), 3.1–3.5 (dd, 2 H), 3.39–3.46 (dd, 2 H), 5.55–5.68 (M, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.2, 23.6, 68.7, 169.4; MS (70 eV), *m/e* (relative intensity) 182 (1), 180 (4, M), 178 (2), 177 (1), 176 (1), 121 (8), 120 (11), 118 (6), 117 (4), 116 (2), 94 (8), 93 (11), 92 (4), 91 (7), 90 (3), 43 (100), 42 (5), 41 (8), 39 (19). Attempted distillation caused decomposition with precipitation of red selenium.

Treatment of 3-Hydroxyselenetane with the Dess–Martin Periodinane. 3-Hydroxyselenetane (0.05 g, 0.37 mmol) was dissolved in chloroform-d_1 (0.5 mL) in an NMR tube (5 mm), and the solution was cooled to −60 °C and mixed with the periodinane[19] (0.20 g, 0.47 mmol) dissolved in chloroform-d_1 (2 mL). The ^{1}H NMR spectrum showed the complete disappearance of the complex absorption of the hydroxyselenetane and the appearance of a new singlet absorption at δ 4.22 corresponding to the 3-ketoselenetane.[26] Similar observations were made on treatment of 3-thietanol with the periodinane. The selenetanone could not be isolated, decomposition occuring on removal of solvent.

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Registry No. 3-Hydroxyselenetane, 73903-64-7; 3-hydroxyselenetane 3,5-dinitrobenzoate, 112422-92-1; 3-phenyl-3-hydroxyselenetane, 112422-88-5; 3-(*p*-methoxyphenyl)-3-hydroxyselenetane, 112422-89-6; 3-ethyl-3-hydroxyselenetane, 112422-90-9; (chloromethyl)oxirane, 106-89-8; 2-(chloromethyl)-2-phenyloxirane, 1005-91-0; 2-(chloromethyl)-2-(*p*-methoxyphenyl)oxirane, 109202-00-8; 2-(chloromethyl)-2-ethyloxirane, 75484-32-1; 1,3-dibromo-2-propanol, 96-21-9; 2-propanol, 67-63-0; 2-phenyl-2-propen-1-ol, 6006-81-1; 2-phenyl-2-propen-1-ol 3,5-dinitrobenzoate, 112422-91-0; 2-phenyl-2-propen-1-ol benzoate, 86148-32-5; 2-(*p*-methoxyphenyl)-2-propen-1-ol, 89619-03-4; 3,5-dinitrobenzoyl chloride, 99-33-2; benzoyl chloride, 98-88-4; 3-acetoxyselenetane, 112422-93-2.

(26) The singlet ^{1}H NMR absorption of the known sulfur analogue, 3-thietanone, appears at δ 4.21.

Improved Syntheses of Substituted Carbazoles and Benzocarbazoles via Lithiation of the (Dialkylamino)methyl (Aminal) Derivatives

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The lithiation of *N*-[(dialkylamino)methyl]carbazoles occurs readily and exclusively at the protonated carbon adjacent to the nitrogen atom. Reaction with a variety of electrophiles produces good to excellent yields of monosubstituted derivatives. Removal of the lithio-directing and nitrogen-protecting function is readily achieved by mild acid-catalyzed hydrolysis during workup of the reaction. Thus, carbazole undergoes lithiation at the 1-position, dibenzo[*c,g*]carbazole at the analogous 6-position, and benzo[*c*]carbazole at both the 6- and 8-positions, with the former predominating. 1,2,3,4-Tetrahydrocarbazole undergoes lithiation at the 8-position, but with 2,3-dimethylindole reaction occurs at the 2-methyl group. Benzo[*a*]carbazole fails to form an aminal derivative, but on direct lithiation in ether it can be substituted exclusively at the 1-position of the fused benzene ring.

Introduction

Although a number of routes are available for the preparation of substituted carbazoles, usually involving either electrophilic addition or ring closure methods,[3] there are few reports of their synthesis via lithiation. Gilman obtained a very poor product yield for the lithiation and subsequent carbonation of carbazole itself,[4] and although higher yields were obtained with *N*-alkylcarbazoles,[5,6] they were still not synthetically useful. Therefore it was generally assumed that the carbazole system did not lithiate very easily. However, more recently it has been shown that very good yields of 1-deuteriocarbazole (**3**) can be obtained from the lithiation of carbazole (**1**)[7] and that in fact the lithiation of carbazole occurs as readily as that of the related tricyclic systems phenothiazine[8] and 5*H*-dibenz[*b,f*]azepine.[9] These observed differences in reactivity were

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