crystallized from methanol–ethyl acetate to afford 11.3 g (0.0557 mol) of amine salt as off-white crystals.

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Registry No.—4-Hydroxyphenylacetonitrile, 14191-95-8; 4-hydroxybenzyl alcohol, 623-05-2; 2-hydroxyphenylacetonitrile, 14714-50-2; 2-hydroxybenzyl alcohol, 90-01-7; 4-hydroxy-3-methoxyphenylacetonitrile, 4468-59-1; 4-hydroxy-3-methoxybenzyl alcohol, 498-00-0; 2-hydroxyphenethylamine HCl, 5136-97-0; 4-hydroxy-3-methoxyphenethylamine HCl, 1477-68-5; NaCN, 143-33-9.

References and Notes

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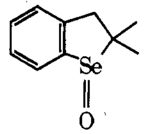
Communications

Organoselenium Chemistry. Intra- and Intermolecular Trapping of Selenenic Acids Formed by Selenoxide Elimination. Formation of a Selenium Ylide

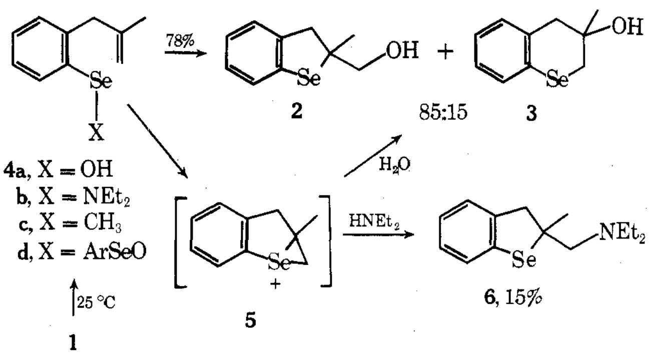
Summary: The thermal decomposition of 3,3-dimethyldihydrobenzoselenophene oxide (1) leads to an unstable intermediate selenenic acid, which is trapped intramolecularly to give hydroxyselenides (2 and 3) or intermolecularly with diethylamine or benzyl bromide to give a selenenamide or selenoxide.

Sir: We report here the thermolysis of the selenoxide 1,[1] which exhibits several striking departures from the behavior of related sulfur compounds.[3] Compound 1 decomposes at room temperature, rapidly in organic solvents, slowly in aqueous solution, giving the alcohols 2 and 3. Similar results are obtained in acidic (acetic acid–dichloromethane, aqueous HCl) or weakly basic (triethylamine- or 1,8-bis(dimethylamino)-naphthalene–dichloromethane, aqueous Na_2CO_3) media.



1

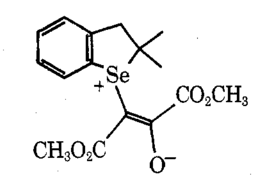
The thermal transformations of 1 are probably initiated by selenoxide syn elimination[4] to selenenic acid **4a.** Evidence for a ring-opened intermediate was obtained by the formation of selenenamide **4b** when 1 was decomposed in the presence of excess diethylamine. The selenenamide was characterized spectroscopically,[5] but could not be isolated in pure form. Reduction ($LiAlH_4$) and methylation of **4b** gave the stable selenide **4c.** *N*,*N*-Dialkylbenzeneselenenamides have been prepared previously by trapping of selenenic acids with amines.[6] Acyclic products were also obtained when decomposition was carried out with strong base and an alkylating agent present (see below). These results are accommodated by a mechanism in which a reactive intermediate (either **4a** or, more probably, the selenenic anhydride[7] **4d,** RSeOSeR or RSe(O)SeR) is trapped either intramolecularly by the olefin, leading to **2** and **3** via an episelenonium ion (**5**),[8] or intermolecularly by amine, with both of these processes being more rapid than the normal disproportionation to diselenide and seleninic acid. Diisopropylamine is evidently too hindered to compete effectively with olefin, since in its presence **1** decomposes to **2** and **3** giving no selenenamide. The selenenamide **4b** in the presence of excess diethylamine slowly isomerizes to **6** in low yield, presumably by reversible hydrolysis to **4a** or **4d,** cyclization to **5,** and capture by amine.[9]



The behavior of 1 is in sharp contrast to the chemistry observed for related sulfur systems. β-Oxygenated sulfides are formed from sulfenic acids, but only in the presence of electrophiles (typically acetic anhydride or acetic acid).[3c,d] In the present study, products of electrophilic double-bond addition (**2, 3,** and **6**) are observed even under basic conditions.

When the decomposition of 1 is carried out in acidic or basic D_2O to test for reversibility of the ring opening, no deuterium incorporation in 2 and 3 could be detected. This demonstrates that the *selenenic acid does not revert to selenoxide* competetively with further transformation. A number of sulfoxide syn eliminations have been shown to be highly reversible under neutral conditions.[3b–h] Even intermolecular olefin additions of sulfenic acids to give sulfoxides can frequently be observed.[3b,h] We have carried out the decomposition of 1 in the presence of ethyl propiolate, phenylacetylene, norbornadiene, or dihydropyran, but have seen no indication of intermolecular reaction with 4a.

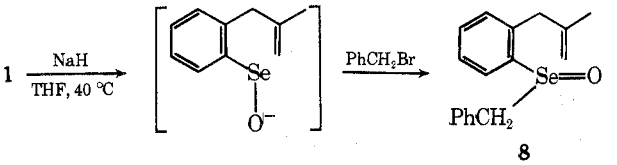
Dimethyl acetylenedicarboxylate reacted rapidly with **1.** The adduct was not the vinyl selenoxide expected from addition of selenenic acid,[3h] but, rather, the ylide **7** formed by direct reaction with selenoxide **1.** Similar ylides have been formed from sulfoxides[10] (although at 100 rather than at 0 °C), as well as from phosphine imides.[11] The much greater rate of



7

reaction of selenoxides compared with that of sulfoxides is reasonably accounted for by the 4–5 pK_a greater basicity of selenoxides.[12] The spectroscopic and analytic properties of **7** are fully compatible with the proposed structure and with the data obtained for analogous sulfur and phosphorus ylides. In particular, the *gem*-dimethyls are diastereotopic and show ^{77}Se–H and ^{77}Se–^{13}C coupling in the proton and carbon NMR spectra,[13] proving that geometry at selenium is pyramidal, and that the five-membered ring is intact.

Decomposition of **1** in the presence of a strong base and an alkylating agent such as benzyl bromide results in the formation of benzyl selenoxide **8**, presumably by Se alkylation of the selenenate ion.[14] This result suggests that the transformation of halides or sulfonates to olefins could be carried out by a selenenate alkylation–selenoxide elimination sequence, perhaps even in a catalytic fashion.



8

Only a few selenenic acids with special substitution have been isolated and characterized.[15] The results reported here, together with previous studies of selenenamide chemistry,[6] point to the emergence of significant differences between selenenic acids and their sulfur analogues.

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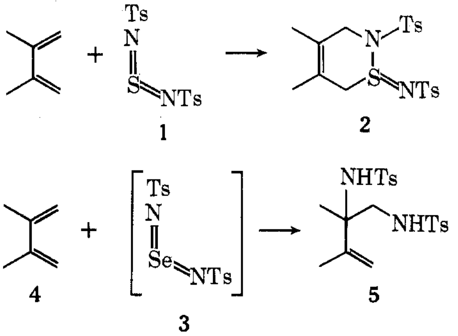
1,2-Diamination of 1,3-Dienes by Imido Selenium Compounds

Summary: Solutions thought to contain the selenium diimide species **3** (TsN=Se=NTs) react with 1,3-dienes to produce 1,2-disulfonamides. In the case of 1,3-cyclohexadiene the sulfonamide groups are introduced cis to each other.

Sir: We have reported that aza analogues (**1** and **3**) of both selenium dioxide[1] and sulfur dioxide[2,3] effect allylic amination of olefins. Since it is well known that the imides of sulfur dioxide (e.g., **1**) readily undergo cycloadditions with dienes to produce stable [4 + 2] adducts (e.g., **2**),[4] we attempted to trap the putative selenodiimide intermediate **3** as its [4 + 2] adduct with 2,3-dimethylbutadiene (**4**). However, only the vicinal disulfonamide **5** could be isolated. This reaction was found to occur with a variety of 1,3-dienes (Table I), and is envisioned as proceeding through the pathway shown in Scheme I for 1,3-cyclohexadiene (**6**). In support of this pathway, hydrogenation (PtO_2, 5 psi H_2 pressure, EtOAc) of the product, disulfonamide **7**,[5a] gave only *cis*-1,2-di(*p*-toluenesulfonamido)cyclohexane.[5b] Exclusive cis stereochemistry



Scheme I