Preparation of Phenylselenoimines from Phenols using Diphenylseleninic Anhydride and Hexamethyldisilazane

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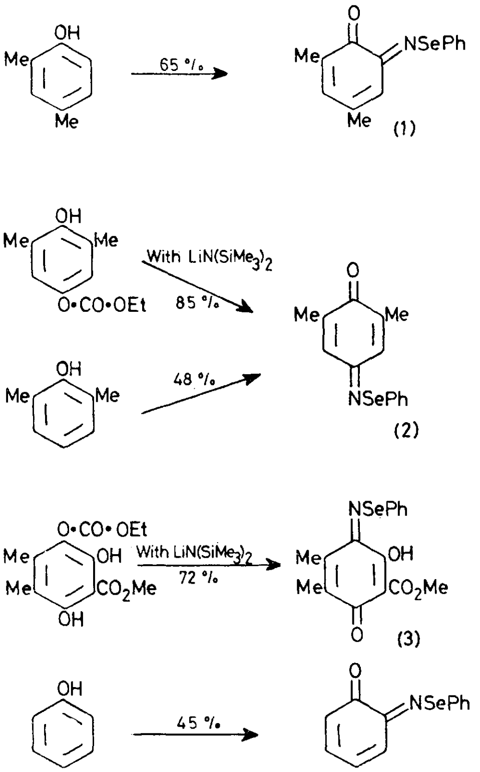
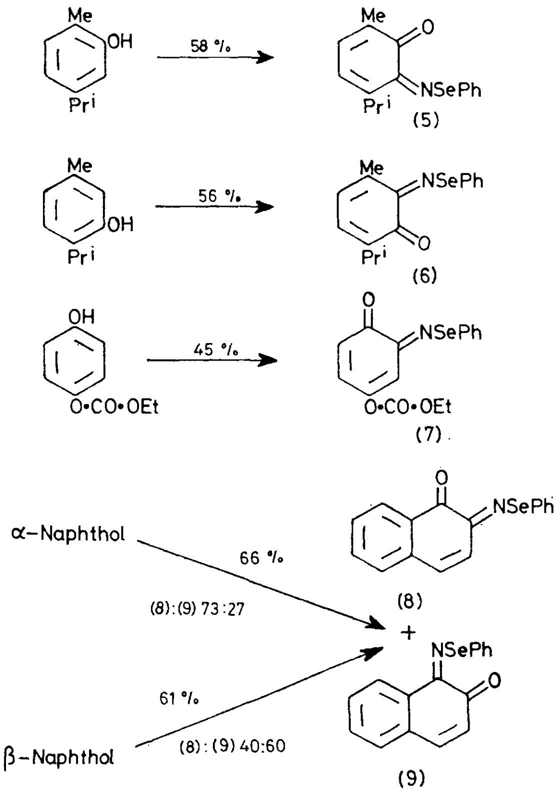
Summary Phenols, on treatment with diphenylseleninic anhydride and hexamethyldisilazane, gave (with a marked preference for *ortho* substitution) the corresponding phenylselenoimines which in turn can be readily reduced to aminophenols.

Recently we have shown that phenols can be conveniently converted into *ortho*-hydroxydienones[1] or *ortho*-quinones[2] by treatment with diphenylseleninic anhydride, PhSe(:O)·O·Se(:O)Ph. We now report the oxidation of phenols with diphenylseleninic anhydride in the presence of hexamethyldisilazane to give good yields of phenylselenoimines. Although the corresponding thioimines are known from a different route[3,4] these selenoimines form a relatively new class of compound.[5]



Scheme 1. Products (**1**)—(**9**) are new compounds giving satisfactory analytical data. (**1**): m.p. 120—121 °C, diacetate m.p. 161—162 °C (ref. 3); λ_{max} 253 (ϵ 9450), 281 (5200), 430 (6820), and 486 nm (14,170). (**2**): m.p. 140—141 °C; λ_{max} 243 (ϵ 13,400), 261 (13,460), 274 (12,600), 356 (2650), and 448 nm (10,900). (**3**): m.p. 132 °C; λ_{max} 263 (ϵ 17,150) and 412 nm (21,300). (**4**): m.p. 75—76 °C, diacetate m.p. 123—124 °C (R. Meldola, G. H. Woolcatt, and E. Wray, *J. Chem. Soc.*, 1896, 1321; λ_{max} 260 (ϵ 3000) and 460 nm (9000). (**5**): m.p. 59—60 °C, diacetate m.p. 228—230 °C; λ_{max} 264 (ϵ 3300), 435 (11,000), and 473 nm (9200). (**6**): m.p. 39—40 °C, diacetate m.p. 164—166 °C; λ_{max} 272 (ϵ 3250), 433 (9600), and 468 nm (10,150). (**7**): m.p. 66—68 °C; λ_{max} 260 (ϵ 5500) 410 (4000), and 464 nm (11,000). (**8**): m.p. 135—136 °C, diacetate m.p. 118—119 °C ('Dictionary of Organic Compounds, Eyre and Spottiswoode, London, (1953); λ_{max} 263 (ϵ, 14,800) 396 (3480), and 498 nm (12,500). (**9**): m.p. 123—124 °C, diacetate m.p. 205—206 °C (R. Meldola and G. T. Morgan, *J. Chem. Soc.*, 1889, 121); λ_{max} 264 (ϵ 11,000), 277 (12,500), and 456 nm (2200). Authentic samples of the diacetates of (**5**) and (**6**) were prepared by nitration of carvacrol and thymol followed by reductive acetylation.



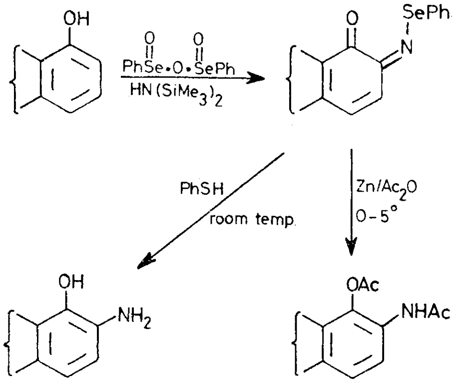
Scheme 2. For details see caption to Scheme 1.

In a general reaction, the phenol (1 equiv.), hexamethyldisilazane (1·2 equiv.), and diphenylseleninic anhydride (1·2 equiv.) were stirred together in benzene for *ca.* 30 min at room temperature. The red selenoimines were isolated by preparative layer chromatography (Scheme 1—3). Changing the solvent to methylene chloride or tetrahydrofuran or the ratio of anhydride to silazane (within limits from 3 : 1 to 1 : 5 mol) does not lead to substantial changes in the yields.

For the majority of the reactions high *ortho*-reactivity was observed. However, in cases in which an unblocked *para*-position was present small quantities (< 10%) of the *para*-imines were also formed.

Reaction of α-naphthol with the silazane and diphenylseleninic anhydride gave a mixture of imines in the ratio

73 : 27 (Scheme 2); corresponding reactions with β-naphthol afforded the same imines however in a different ratio, 40 : 60.



Scheme 3

In order to test for the possible intermediacy of *ortho*-quinones in these reactions 1,2-naphthoquinone gave the above imines (65%) in a 75 : 25 ratio. However, in other examples the *ortho*-quinones were excluded as intermediates. Thus thymo-1,2-quinone[2] failed to produce imines under the usual conditions, a result consistent with the observation that quinones are usually formed at higher temperatures.[2]

The use of ammonia or tris(trimethylsilyl)amine in place of hexamethyldisilazane gave only trace amounts of selenoimines.

Many of the selenoimines were reductively acetylated, using zinc and acetic anhydride, to the known aminophenol diacetates (Schemes 1—3). The phenylselenoimine from 2,4-xylenol was smoothly converted into the 6-aminophenol at room temperature by reduction with benzenethiol. The reactions described, therefore, constitute a mild amination procedure for phenols.

We are currently investigating the mechanistic aspects of phenylselenoimine formation. Since the disilazane does not react with phenols, it must react with the diphenylseleninic anhydride to give a more reactive reagent.

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