FIRST STABLE SELENABENZENE ANALOGUE, 2-CYANO-1-METHYL-4-PHENYL-1-SELENANAPHTHALENE: SYNTHESIS AND REACTIONS

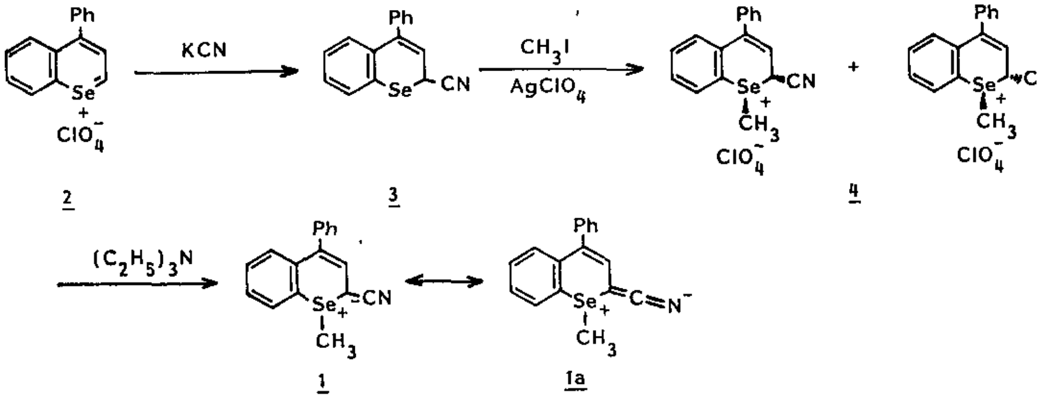
Mikio Hori,* Tadashi Kataoka, Hiroshi Shimizu, Kazuhiro Tsutsumi, and Shinya Imaoka
Gifu Pharmaceutical University, 6-1, Mitahora-higashi 5-chome, Gifu 502, Japan

Abstract - 2-Cyano-1-methyl-4-phenyl-1-selenanaphthalene (1) was synthesized as the first isolable selenabenzene. Its ylidic structure was characterized by the spectral and chemical evidence. The thermal reaction of the selenanaphthalene 1 afforded [1,2]- (5) and [1,4]-rearranged products (6) together with dimeric compounds 7. The photochemical reaction afforded the different [1,4]-rearranged product, ketenimine 9 and the photo-oxygenated product, 4-phenylcoumarin (10).

Stable thiabenzenes have been synthesized and their reactivities have been extensively investigated,[1] but the selenium-analogues, selenabenzenes, have not been isolated yet. Mislow and his co-workers reported that selenabenzenes are ylidic and less stable than thiabenzenes.[2] We now report synthesis and reactions of the first isolable selenabenzene analogue stabilized by a cyano group, i.e. 2-cyano-1-methyl-4-phenyl-1-selenanaphthalene (1).

The synthetic route is shown in Scheme 1. 4-Phenyl-1-selenanaphthylium perchlorate (2)[3] reacted with potassium cyanide in dichloromethane to give 2-cyano-4-phenyl-1-selenochrom-3-ene (3) in 98 % yield. The ^{1}H nmr spectrum of 3 showed two doublets at δ 4.30 and 5.90 assigned to H(2) and H(3), respectively. Methylation of 3 with methyl iodide in the presence of silver perchlorate afforded selenonium salt 4 in 89 % yield. The ^{1}H nmr spectrum showed two singlets at δ 3.24 and 3.34 due to the Se-methyl groups. This indicates that the compound 4 is an inseparable mixture of cis- and trans-isomers based on the pyramidal inversion of the selenium atom. The signal of the methyl group in cis-4 appears at lower field (δ 3.34) than that in trans-4 (δ 3.24) because of the anisotropic effect of the cyano group. The isomer ratio was trans/cis = 1.1.

The selenonium salt 4 was treated with triethylamine in ethanol at 0°C to give the selenanaphthalene 1 as orange prisms, mp 114-115°C (decomp.), in 85 % yield. The ^{1}H nmr spectrum showed the signals at δ 2.23 (3H, s, CH_3), 6.74 (1H, s, H(3)), and 7.05-7.58 (9H, m, aromatic H), and its ir spectrum had a lower-shifted strong absorption band at 2140 cm^{-1} due to the cyano group. These spectral data indicate that the selenabenzene is an ylide and the ylidic carbanion is

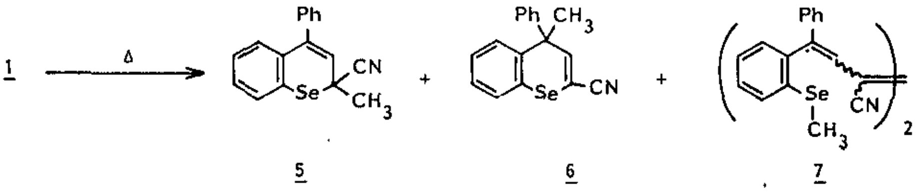


Scheme 1

delocalized over the cyano group (1a in Scheme 1). Treatment of 1 with perchloric acid gave the selenonium salt 4.

The selenanaphthalene 1 was refluxed in dry benzene for 24 h under nitrogen atmosphere to give 2-cyano-2-methyl-4-phenyl-1-selenochromene (5) and 2-cyano-4-methyl-4-phenyl-1-selenochromene (6) in 18 and 11 % yields, respectively. The physicochemical data of 5 and 6 were as follows: compound 5: oil; ^{1}H nmr (δ, ppm) 1.94 (3H, s, CH$_3$), 5.68 (1H, s, H(3)), 7.05-7.60 (9H, m, aromatic H); ^{13}C nmr (δ, ppm) 25.6 (CH$_3$), 26.2 (C(2)), 121.2 (CN), 123.8, 127.1, 127.2, 128.3, 129.0, 129.1, 129.7, 130.2, 133.8, 140.0 (aromatic C), 145.0 (C(3)), 151.0 (C(4)); ir (ν, cm^{-1}) 2230 (CN); high resolution ms calcd. $C_{17}H_{33}NSe$. (m/z) 311.0209. found (m/z) 311.0182. Compound 6: mp 84.5-86°C as colorless prisms; ^{1}H nmr (δ, ppm) 1.86 (3H, s, CH$_3$), 7.08-7.49 (10H, m, olefinic and aromatic H); ^{13}C nmr (δ, ppm) 26.5 (CH$_3$), 49.6 (C(4)), 103.1 (CN), 127.0, 127.3, 128.0, 128.3, 128.7, 139.7 (aromatic C), 145.4 (C(2)), 151.1 (C(3)); ir (ν, cm^{-1}) 2210 (CN); ms (m/z) 311 (M$^+$, Se = 80); Anal. $C_{17}H_{33}NSe$. Other products were too complex to be isolated.

Furthermore, thermal reactions of 1 in the presence of 0.1 molar equivalents of the compounds carrying an active hydrogen afforded the dimeric compounds 7 in addition to 5 and 6 as shown in Scheme 2 and Table 1.



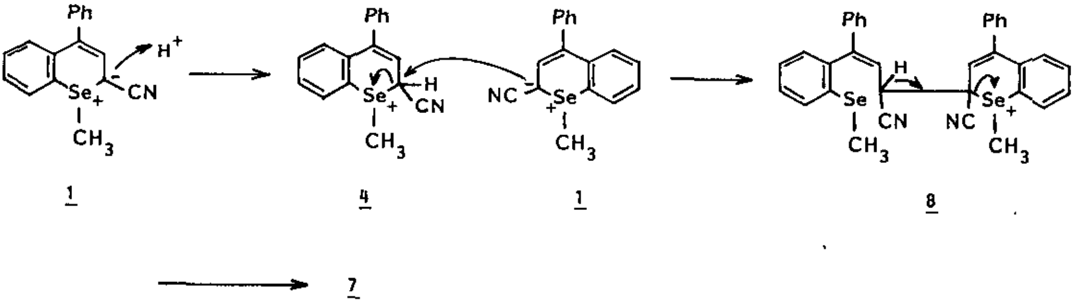
Scheme 2

Table 1. Thermal Reactions of Selenanaphthalene 1

Solvent	Reagent	Yield (%)		
		5	6	7
C_6H_6	—	18	11	–
C_6H_6	malononitrile	17	9	18
C_6H_6	succinimide	15	17	20
C_2H_5OH	—	18	9	9
$CHCl_3$	*selenonium salt 4*	33	2	21

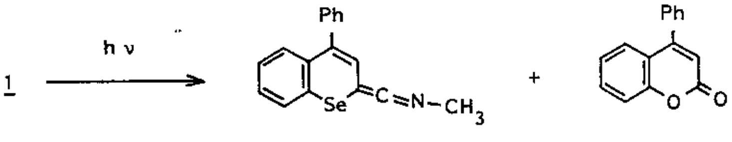
One dimeric compound 7a was determined as the trans-dimer, ^1H nmr spectrum of which showed the signals at δ 2.25 (6H, s, CH_3 x 2), 7.00-7.60 (20H, m, olefinic and aromatic H). Another compound 7b was determined as the cis-dimer because it was isomerized to 7a by heating at 235°C or by treatment with silica gel. Since 7b easily changed to 7a during the purification, it was not isolated in a pure form. Its ^1H nmr spectrum showed two singlets at δ 2.18 and 2.25 assigned to two methyl groups. And its fragmentation pattern of the EI-ms spectrum was in good agreement with that of the trans-isomer 7a.

In this case, a plausible mechanism for the dimerization is shown in Scheme 3. A small amount of 1 would be protonated by the compounds bearing an active hydrogen to form the selenonium ion 4. The ylidic carbanion of 1 would then attack nucleophilically at C(2) of 4 followed by ring opening of 4. The resulting dimeric intermediate 8 would undergo ring opening and subsequent proton removal to form the dimers 7a-b. Actually, we have examined the reaction of the selenanaphthalene 1 with 0.3 molar equivalents of 4 and obtained the dimeric compounds 7 in 21 % yield.



Scheme 3

Finally, we have investigated the photoreaction of 1. Selenanaphthalene 1 was irradiated with a 400 W high-pressure mercury lamp at room temperature for 8 h to give a [1,4]-rearranged product, ketenimine 9 and unexpected product, 4-phenylcoumarin (10) in 17 and 11 % yields, respectively, as shown in Scheme 4. A few examples of ketenimine formation have been reported in the thermal [2,3]-sigmatropic rearrangement of cyano-stabilized sulfur ylides.[4] Our finding is the first case

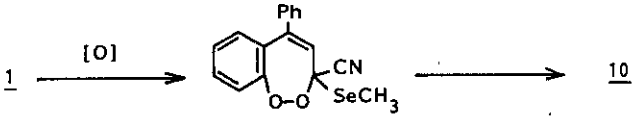


9

10

Scheme 4

of ketenimine formation by [1,4]-rearrangement. The structure of 9 was determined by the following physicochemical data: ^{1}H nmr (δ , ppm) 2.37 (3H, s, CH_3), 7.20-7.90 (10H, m, olefinic and aromatic H); ^{13}C nmr (δ , ppm) 7.2 (CH_3), 124.4, 127.1, 128.6, 129.5, 129.7, 130.0, 131.2, 131.6, 131.7, 132.5, 134.4, 134.6, 137.7 (olefinic and aromatic C), 196.7 (=C=); high resolution ms calcd. $C_{17}H_{33}NSe$. (m/z) 311.0209. found (m/z) 311.0208. On the other hand, the structure of 10 has been determined by comparison of its ^{1}H nmr, ir, and ms spectra with those of an authentic sample.[5] Formation of 10 presumably proceeds via the peroxide 11 as shown in Scheme 5. Further investigation of this photo-oxygenation is now going on and will be described in a full paper.



11

Scheme 5

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