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

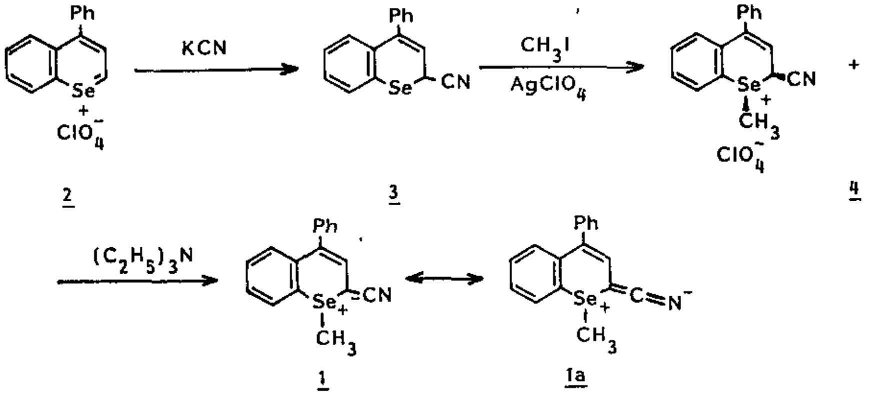
Mikio Hori,* Tadashi Kataoka, Hiroshi Shimizu, Kazuhiro Tsutsumi, and Shinya Imaoka
Gifu Pharmaceutical University, 6-1, Mitahora-higashi 5-chome, Gifu 502, Japan

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

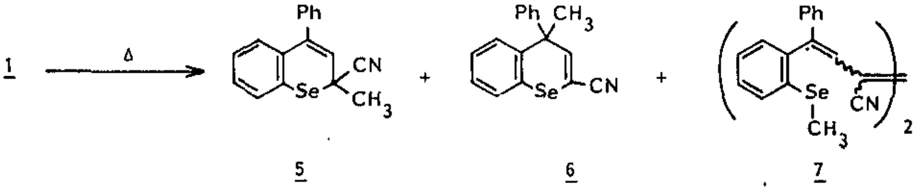


Scheme 1

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.



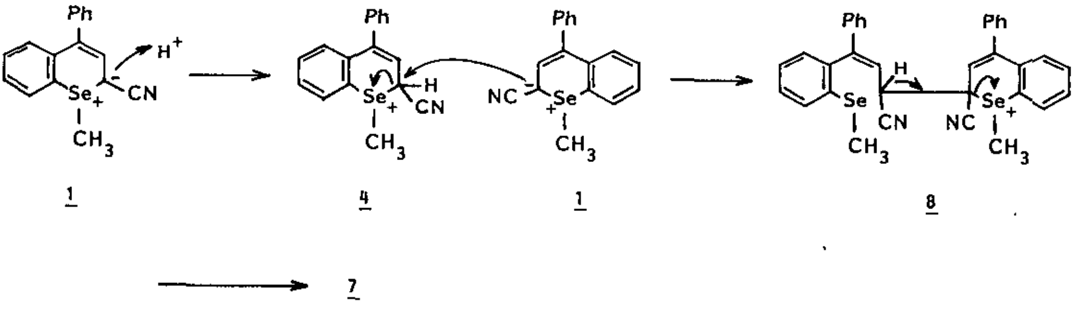
Scheme 2

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

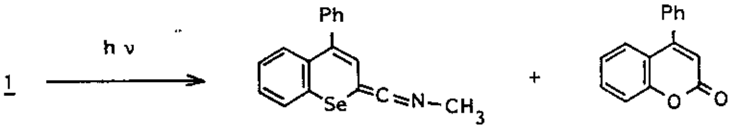
One dimeric compound 7a was determined as the trans-dimer, ^1H nmr spectrum of which showed the signals at δ 2.25 (6H, s, CH_3 x 2), 7.00-7.60 (20H, m, olefinic and aromatic H). Another compound 7b was determined as the cis-dimer because it was isomerized to 7a by heating at 235°C or by treatment with 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

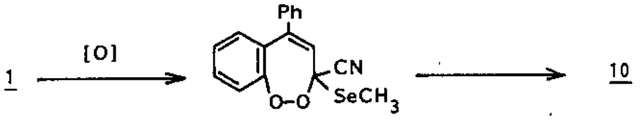
Finally, we have investigated the photoreaction of 1. Selenanaphthalene 1 was irradiated with a 400 W high-pressure mercury lamp at room temperature for 8 h to give a [1,4]-rearranged product, ketenimine 9 and unexpected product, 4-phenylcoumarin (10) in 17 and 11 % yields, respectively, as shown in 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

REFERENCES

1. M. Hori, "Organic Sulfur Chemistry", ed. by R. Kh. Freidlina, Pergamon Press, New York, 1981, pp. 81; M. Hori and T. Kataoka, Yuki Gosei Kagaku Kyokai Shi, 1987, 45, 232.
2. J. Stackhouse, G. E. Senkler, Jr., B. E. Maryanoff, and K. Mislow, J. Am. Chem. Soc., 1974, 96, 7835.
3. A. Tadino, L. Christieaens, and M. Renson, Bull. Soc. Roy. Sci. Liege, 1973, 42, 129.
4. G. Morel, S. Khamsitthideth, and A. Foucaud, J. Chem. Soc. Chem. Comm., 1978, 274; G. Morel, M. A. LeMoing-Orlic, S. Khamsitthideth, and A. Foucaud, Tetrahedron, 1982, 38, 527.
5. F. Bergmann, M. Weizmann, E. Dimant, J. Patai, and J. Szmuskowicz, J. Am. Chem. Soc., 1948, 70, 1612; U. K. Pandit and I. P. Dirk, Tetrahedron Lett., 1963, 891.

Received, 4th June, 1987