Thermal Formation of Triphenodithiazinequinone and Triphenodiselenazinequinone

Hisao Nishi, Satoshi Minami, and Kiyoshi Kitahara*

Department of Applied Chemistry, Faculty of Engineering, Saitama University,
Urawa 338, Japan

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Thermal treatment of 2,5-bis(2-thioanisidino)-3,6-dichloro-1,4-benzoquinone and its selenium derivative brought about demethylchlorination to give triphenodithiazinequinone and triphenodiselenazinequinone, respectively.

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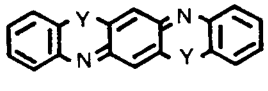
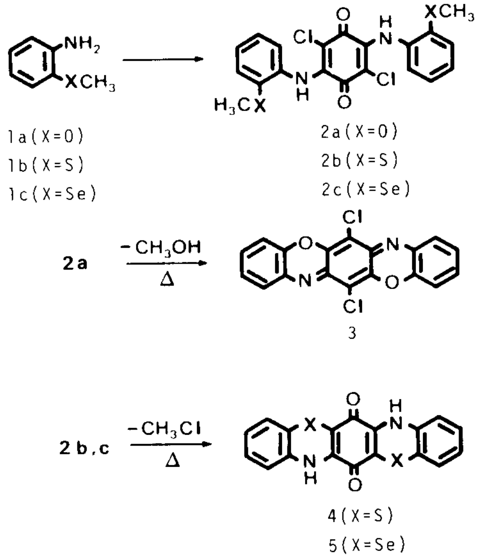


(Y=O , S)

Scheme



Triphenodioxazines (Y = O) and triphenodithiazines (Y = S) are useful dyes and pigments [1]. In a previous paper [2], we have reported a new synthesis of triphenodithiazines and triphenodithiazinequinones **4**. Compounds **4** were sparingly soluble in organic solvents and showed high decomposition points. Some of the compounds **4** were expected to be used for optical recording material as near infrared absorbing pigments [3]. We report now the thermal formation of **4** and its selenium derivative, triphenodiselenazinequinone (**5**). Synthetic routes are shown in the Scheme. *o*-Selenoanisidine (**1c**) was prepared from zinc 2-aminobenzeneselenolate [4] with methyl iodide in the presence of a phase transfer catalyst such as tetrabutylammonium bromide. Intermediates **2a-c** were obtained by the condensation of chloranil with *o*-anisidine (**1a**), *o*-thioanisidine (**1b**) or **1c** in a 1:2 molar ratio. Treatment of **2a** in a high boiling solvent gave 6,13-dichlorotriphenodioxazine (**3**) by demethanolation [5]. On the other hand, as the color of **2b** changed brown to blue by heating, the thermal behavior was investigated in solid phase by TG-DTA in a nitrogen atmosphere at a heating rate of 10°/minute. The TG-DTA curves for **2b** are showed in the Figure. After the endothermic curve corresponding to the melting point of **2b** is observed, the weight loss at 210-280° reaches 21.9% which approximately agrees with the calculated value of 22.4% for the elimination of two moles of methyl chloride from **2b**. Treatment of **2b** in refluxing *N*-methyl-2-pyrrolidone did not afford **3** but **4**. The ms and elemental analysis consist of molecular formula $C_{18}H_{10}N_2O_2S_2$. The ir shows a NH stretching band and a C=O stretching band at 3240 and 1630 cm^{-1}, respectively. It is assumed that this thermal reaction proceeded by the cleavage of the CH_3-S bond of **2b**. Alkyl aryl sulfides are cleavaged by metal-amine systems to give the aromatic thiols [6]. However, the thermal cleavage of these sulfides for the formation of heterocyclic compounds seems not to have been reported. In the case of **2c**, a similar thermal behavior was observed to produce **5**. The visible spectrum of **5** in sulfuric acid showed a bathochromic shift compared with that of **4**.

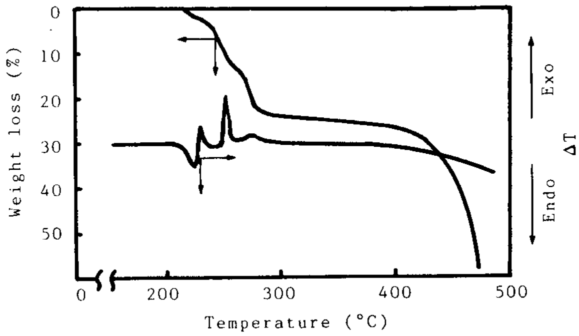


Figure. TG-DTA curves for compound **2b**.

EXPERIMENTAL

Melting points, decomposition points and the thermal properties were measured by the use of Rigaku TG-DTA. The ir, ms, ^{1}H-nmr and electronic absorption spectra were recorded by means of a JASCO IRA-2, a JEOL JMS-01SG-2, a JEOL PMX60Si and a Hitachi ESP-3T spectrometers, respectively.

Materials.

Compounds **1b** [7], **2b** [2] and **2c** [2] were prepared according to references. Compound **2b** was brown needles from chlorobenzene, yield 55%, mp 218°. Compound **2c** was brown needles from chlorobenzene, yield 36%, mp 228°.

o-Selenoanisidine **1c**.

A solution of zinc 2-aminobenzeneselenolate (2.0 g, 4.9 mmoles) in 1*M* aqueous sodium hydroxide (30 ml) was refluxed under a nitrogen atmosphere until the solids were dissolved. After cooling, methyl iodide (2.0 g, 14.1 mmoles), tetrabutylammonium bromide (0.4 g, 1.2 mmoles) and benzene (40 ml) were added. The mixture was refluxed for 3 hours. The benzene layer was washed with water, dried over calcium chloride, filtrated and evaporated *in vacuo*. The resulting residue was distilled under reduced pressure at 71-74°/3 torr to give a colorless oil (1.1 g, 60%); ^{1}H-nmr (deuteriochloroform): 2.2 (s, 3H, CH_3), 4.2 (br, 2H, NH_2), 6.6-7.5 (m, 4H, aromatic).

Triphenodithiazinequinone **4**.

A solution of **2b** (0.23 g, 0.5 mmole) in *N*-methyl-2-pyrrolidone (6 ml) was refluxed for 5 hours. The precipitate was filtered off, washed with hot DMF, acetone and water, dried to give **4** as a blue powder (0.14 g, 77%); ms: (m/z) 350 (M^+); vis (sulfuric acid): λ max 723 nm.

Anal. Calcd. for $C_{18}H_{10}N_2O_2S_2$: C, 61.69; H, 2.88; N, 8.00. Found: C, 61.55; H, 2.90; N, 7.85.

Triphenodiselenazinequinone **5**.

According to the above procedure, **5** was obtained as a blue powder in a yield of 41%; ms: (m/z) 444 (M^+); ir (potassium bromide): 3270 (NH), 1633 (C=O) cm^{-1}; vis (sulfuric acid): λ max 740, 800 nm.

Anal. Calcd. for $C_{18}H_{10}N_2O_2Se_2$: C, 48.67; H, 2.27; N, 6.21. Found: C, 48.43; H, 2.18; N, 6.18.

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