Heteroatom Chemistry
Volume 4, Number 4, 1993

Synthesis of 1λ⁴,2-Diselenol-1-ylium Salts*

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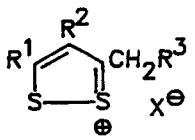
Received 27 October 1992

ABSTRACT

Seven bis-(1λ⁴,2-diselenol-1-ylium) tetrachloroferrates have been prepared by reaction of 1,3-diketones or 1,3-ketoaldehydes with hydrogen selenide and iron(III) chloride in ethanol saturated with hydrogen chloride. They decompose gradually in air. The corresponding 1λ⁴,2-diselenol-1-ylium perchlorates have been prepared by reaction of the tetrachloroferrates with perchloric acid in acetic acid and are stable. The tetrachloroferrates react with benzenediazonium tetrafluoroborate to give 6,6aλ⁴-diselena-1,2-diazapentalenes.

INTRODUCTION

1λ⁴,2-Dithiol-1-ylium salts (**1**) are versatile starting materials for the synthesis of 1,6,6aλ⁴-triheterapentalenes (**2**) (Z = O, S, Se, NR) [1–3] and their 2-aza analogues (**3**) (Z = 0, NAr) [4,5]. In connection with our interest in selenium-containing heterocycles, we considered the possibility of using 1λ⁴,2-diselenol-1-ylium salts as starting materials for the synthesis of selenium-containing 1,6,6aλ⁴-triheterapentalenes, very few of which have been prepared. However, at the beginning of our work, only four 1λ⁴,2-diselenol-1-ylium salts had been reported, namely, the 3,5-diamino derivatives (**4a**) and (**4b**), obtained by oxidation of diselenomalonamide with iron(III) chloride or with iodine, respectively [6], and the 3,5-dimethyl derivates (**5a**) and (**5b**) [7].



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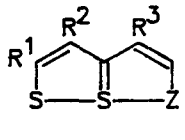

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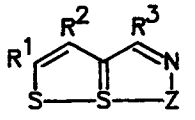

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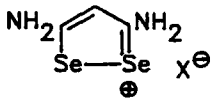
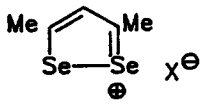


(4a) X=Cl

(4b) X=I



(5a) X=I

(5b) X=1/2CoCl$_4$

STRUCTURE 1

The salts (**5a**) and (**5b**) were obtained by the reaction of pentan-2,4-dione with hydrogen selenide in the presence of an oxidizing agent, the use of ethyl iodide and nickel carbonate giving the iodide (**5a**) and cobalt(II) carbonate giving the tetrachlorocobaltate (**5b**). This article reports the results of detailed studies of the preparation of a series of bis-(1λ⁴,2-diselenol-1-ylium) tetrachloroferrates (**6a**)–(**6g**) and the corresponding perchlorates (**7a**)–(**7g**), following our earlier mention of unpublished work [4,5].

*Studies of heterocyclic compounds, Part 30.
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1042-7163/93/$5.00 + .25

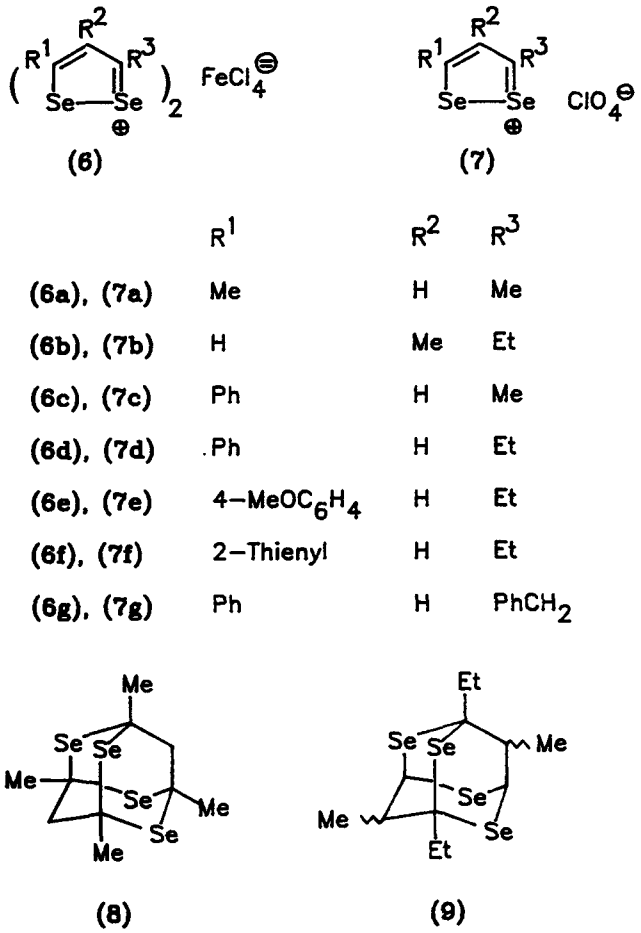
RESULTS AND DISCUSSION

The tetrachloroferrates (**6a**)–(**6g**) were prepared by reaction of the appropriate 1,3-diketones or 1,3-ketoaldehyde with hydrogen selenide and iron(III) chloride in ethanol saturated with hydrogen chloride. Control experiments showed that the yield and purity of the tetrachloroferrates (**6b**), (**6c**), and (**6g**) depended on the iron(III) chloride-diketone ratio. The optimum ratio for the preparation of these salts was found to be 2:1 and was adopted generally, giving yields of the tetrachloroferrates (**6a**)–(**6g**) in the range 34–68%. Further increase of the iron(III) chloride-diketone ratio resulted in progressively increased contamination of the salts (**6a**)–(**6g**) with selenium.

The reaction leading to the tetrachloroferrate (**6a**) also gave in substantial amount a homogeneous neutral crystalline product whose elemental analysis, ^{1}H NMR spectrum (CH_3 singlet at δ 1.96, CH_2 singlet at δ 1.99) and mass spectrum (M^+ cluster centred at *m/e* 454), was consistent with the tetraselenaadamantane structure (**8**). The tetrachloroferrate (**6b**) also was accompanied by a neutral crystalline product whose elemental analysis and mass spectrum (M^+ cluster centred at *m/e* 482) corresponded with the tetraselenaadamantane structure (**9**), but this product melted over a wide range (159–196°C) and its ^{1}H NMR spectrum was complex, indicating that it consisted of at least two pairs of diastereoisomers.

The diselenolylium ions in the salts (**6a**)–(**6g**) could be formed from hydrogen selenide by two feasible routes. In the first route, hydrogen diselenide (H_2Se_2) could be formed by oxidation of hydrogen selenide by the iron(III) chloride and subsequently undergo acid-catalyzed condensation at the carbonyl groups of the 1,3-diketone or ketoaldehyde, analogously to the reaction of hydrogen disulfide with 1,3-diketones which gives 1λ^4,2-dithiol-1-ylium salts [1]. Although hydrogen diselenide has never been isolated, its alkali metal salts are well known [8,9] and it is possible that hydrogen diselenide could be formed and react in situ to give the tetrachloroferrates. Alternatively acid-catalyzed conversion of the diketones to the corresponding diselenones could take place first, followed by Se-Se oxidative coupling effected by the iron(III) chloride to form the diselenolylium ions. The isolation of the tetraselenaadamantanes (**8**) and (**9**) is good evidence that diselenones are reaction intermediates, dimerisation of which would give the corresponding tetraselenaadamantanes, e.g., 2 $CH_3 \cdot CSe \cdot CH_2 \cdot CSe \cdot CH_3 \rightarrow$ (**8**) and 2 $CH_3CH_2 \cdot CSe \cdot CH(CHSe)CH_3 \rightarrow$ (**9**), but it is not certain that diselenones are intermediates on the route to the diselenolylium cations.

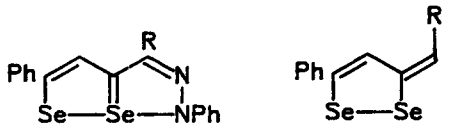
The tetrachloroferrates (**6a**)–(**6g**) are unstable and gradually decompose in the solid state to give intractable and largely insoluble material. Evidence of decomposition is noticeable several days after preparation and is complete after several weeks as shown by nonformation of purple coupling products when treated with benzenediazonium tetrafluoborate (vide infra). The corresponding perchlorates (**7a**)–(**7g**), prepared by treatment of the tetrachloroferrates (**6a**)–(**6g**) with 70% perchloric acid, were stable. The source of instability thus lies in the presence of the tetrachloroferrate ion and possibly involves slow oxidation of the tetrachloroferrate ion by atmospheric oxygen.



	R^1	R^2	R^3
(**6a**), (**7a**)	Me	H	Me
(**6b**), (**7b**)	H	Me	Et
(**6c**), (**7c**)	Ph	H	Me
(**6d**), (**7d**)	Ph	H	Et
(**6e**), (**7e**)	4–$MeOC_6H_4$	H	Et
(**6f**), (**7f**)	2–Thienyl	H	Et
(**6g**), (**7g**)	Ph	H	$PhCH_2$

STRUCTURE 2

The tetrachloroferrates (**6c**) and (**6d**) reacted with benzenediazonium tetrafluoroborate in ethanol to give the purple 6,6aλ^4-diselena-1,2-diazapentalenes (**10a**) and (**10b**), respectively. Formation of compounds (**10a**) and (**10b**) is presumed to take place by reversible deprotonation of the salts (**6c**) and (**6d**) by the solvent to give equilibrium concentrations of the 3-methylene-3*H*-1,2-diselenoles (**11a**) and (**11b**), respectively, which undergo rapid electrophilic substitution to give compounds (**10a**) and (**10b**). 3-Methylene-3*H*-1,2-diselenoles are unstable. Attempts to isolate 3-methylene-3*H*-1,2-diselenoles by deprotonation of the salts (**6a**)–(**6d**) or



(10a) R=H (11a) R=H

(10b) R=Me (11b) R=Me

STRUCTURE 3

(**7a**)–(**7d**) with aqueous sodium carbonate or with triethylamine in dichloromethane were unsuccessful and gave ill-defined decomposition products together with selenium.

EXPERIMENTAL

Melting points were determined with a Kofler hot-stage apparatus. ^{1}H NMR spectra were determined at 200.13 MHz and ^{13}C NMR spectra at 50.32 MHz with a Bruker AC 200 spectrometer. ^{1}H NMR chemical shifts are given in parts per million downfield from tetramethylsilane as internal reference. Unless otherwise stated, δ values refer to singlet absorptions. Data are given in the following order: δ value, number of protons, multiplicity (d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), J (Hz), and assignment. ^{13}C NMR chemical shifts are given relative to the central deuteriochloroform peak taken as δ 77.00 and are proton-decoupled values.

Extracts were dried over sodium sulfate. Solvents were removed from extracts and chromatographic eluates at reduced pressure with a rotary evaporator. Ether denotes diethyl ether. Petroleum denotes a pentane-hexane mixture of boiling range 40–60°C. Acetic acid was redistilled. The following solvents were dried by standard procedures and redistilled before use: acetonitrile, benzene, cyclohexane, ethanol, ether, hexane, methanol, and petroleum. Perchloric acid refers to 70–72% (w/w) perchloric acid. Column chromatography was carried out with alumina (activity II, pH ca. 9.5, 70–230 mesh) or silica (85–200 mesh). The following abbreviations are used: B = benzene, H = hexane, and P = petroleum.

Preparation of 1,3-Diketones

Pentan-2,4-dione and 1-phenylbutan-1,3-dione were commercially available materials. 2-Methyl-3-oxobutanal [3] and 1-phenylpentan-1,3-dione [10] were prepared as in the references cited.

1,4-Diphenylbutan-1,3-dione. This ketone was prepared by the method of Hauser [10,11] using acetophenone (117 mL, 1 mole), ethyl phenylacetate (239 mL, 1.5 moles), sodium (46 g, 2 moles), liquid ammonia (1 L), and ether (500 mL). After purification via its copper salt, using copper(II) acetate (90.8 g, 0.5 mole) in water (750 mL) and recrystallization from ethanol-ether (9:1), the ketone (146.8 g, 61.6%) was obtained as colorless crystals, mp 54°C (Ref. [12] 51–52.5°C).

1-p-Methoxyphenylpentan-1,3-dione. This ketone was prepared according to the method cited [10,11], using *p*-methyoxyacetophenone (30.04 g, 200 mmol), ethyl propionate (34.4 mL, 300 mmol), sodium (9.2 g, 400 mmol), liquid ammonia (400 mL), and ether (200 mL). After purification via the copper salt using copper(II) acetate (24 g, 120 mmol) in water (300 mL) followed by distillation, the ketone was obtained as a pale yellow oil (25.3 g, 61%), bp 156–159°C/1 mm Hg; ^{1}H NMR ($CDCl_3$) δ 1.20 (3H, t, J 7.6, 5-Me), 2.43 (2H, q, J 7.6, 4-CH_2), 3.85 (3H, OMe), 6.11 (2-CH_2), 6.89 and 6.97 (2H, 2*m*-protons of Ar), 7.81 and 7.89 (2H, 2 *o*-protons of Ar); ^{13}C NMR ($CDCl_3$) δ 9.73 (5-Me), 31.71 (4-CH_2), 55.22 (OMe), 94.25 (2-CH_2), 113.72, 128.88, 130.88, 162.87 (4 × Ar-C), 183.77 (1-CO), 195.75 (3-CO). Anal. calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 70.16; H, 7.26%.

1,2'-Thienylpentan-1,3-dione. This ketone was prepared according to the method cited [10,11] using 2-acetylthiophene (5.40 mL, 50 mmol), ethyl propionate (8.61 mL, 75 mmol), sodium (2.3 g, 100 mmol), liquid ammonia (50 mL), and ether (50 mL). Purification was effected via the copper salt using copper(II) acetate (6 g, 30 mmol) in water (100 mL). Distillation gave the ketone as a pale yellow oil (4.15 g, 46%), bp 150–160°C/1 mm Hg (heating block); ^{1}H NMR ($CDCl_3$) δ 1.20, (3H, t, J 7.5, 5-Me), 2.39 (2H, q, J 7.5, 4-CH_2), 6.03 (2H, 2-CH_2), 7.09–7.15 (1H, m, 4'-H), 7.57–7.69 (1H, m, 3'-H), 7.69–7.74 (1H, m, 5'-H); ^{13}C NMR ($CDCl_3$) δ 9.98 (5-Me), 30.45 (4-CH_2), 94.86 (2-CH_2), 128.10, 130.00, 132.16, 141.58 (4 × thiophene-C), 181.63 (1-CO), 191.54 (3-CO). Anal. calcd for $C_9H_{10}O_2S$: C, 59.32; H, 5.53. Found: C, 59.15; H, 5.38%.

Preparation of Bis-(1λ⁴,2-diselenol-1-ylium) Tetrachloroferrates

The following general procedures were used.

Procedure A. Hydrogen selenide was generated slowly during 4 hours by dropwise addition of 6 M hydrochloric acid to crushed aluminum selenide (58 g, 200 mmol) in a nitrogen atmosphere. The hydrogen selenide was carried in a slow stream of nitrogen into a stirred solution of the 1,3-diketone or 1,3-ketoaldehyde (150 mmol) and iron(III) chloride (16.2 g, 100 mmol) in ethanol saturated with hydrogen chloride (150 mL), cooled to 0°C. After 4 hours the mixture was diluted with ether (2

L) and the precipitated salt was filtered off, washed successively with much ether, benzene, and ether, dried, and recrystallized from ethanol saturated with hydrogen chloride. The reaction filtrates were combined with the ether and benzene washings. The resulting solution was washed repeatedly with water to remove hydrochloric acid and dried, and solvent was removed. Subsequent workup varied and is given for individual cases.

Procedure B. Hydrogen selenide was generated slowly over 4 hours by dropwise addition of water (10 mL) and latterly 6 M hydrochloric acid (25 mL) to crushed aluminum selenide (5.8 g, 20 mmol) in a nitrogen atmosphere and carried in a slow stream of nitrogen into a stirred solution of the diketone (15 mmol) and iron(III) chloride (4.87 g, 30 mmol) in ethanol saturated with hydrogen chloride, cooled to 0°C, The mixture was then diluted with much ether, and the precipitated salt was filtered off and washed repeatedly with portions of ether-benzene (1:1). The solid was collected, slurried with benzene, filtered off, and washed with ether, then dried and recrystallized from ethanol saturated with hydrogen chloride.

Bis-(3,5-dimethyl-1λ⁴,2-diselenol-1-ylium) Tetrachloroferrate (**6a**). Compound (**6a**) (16.5 g, 34%) was obtained (procedure A) from pentan-2,4-dione (15.4 mL) as deep violet prisms, mp 95–97°C. Anal. calcd for $C_{10}H_{14}Cl_4FeSe_4$: C, 18.54; H, 2.18. Found: C, 18.70; H, 2.25%. The residue from the mother liquors was recrystallized from cyclohexane to give 1,3,5,7-tetramethyl-2,4,6,8-tetraselenaadamantane (**8**) (6.91 g, 20%) as white needles, mp 165–166°C; ^{1}H NMR ($CDCl_3$) δ 1.96 (12H, Me), 1.99 (4H, CH_2); M^+ at *m/e* 454. Anal. calcd for $C_{10}H_{16}Se_4$: C, 26.57; H, 3.57. Found: C, 26.9; H, 3.7%.

Bis-(3-ethyl-4-methyl-1λ⁴,2-diselenol-1-ylium) Tetrachloroferrate (**6b**). Compound (**6b**) (19.47 g, 38.4%) was obtained (procedure A) from 2-methyl-3-oxobutanal [3] (17.12 g) as purple needles, mp 76–79°C. Anal. calcd for $C_{12}H_{18}Cl_4FeSe_4$: C, 21.33; H, 2.68. Found: C, 21.47; H, 2.88%. The gummy residue from the mother liquors was chromatographed [alumina (35 × 3.5 cm)]. The initial eluates [PB (1:1), 450 mL] were discarded, and the succeeding eluates [B, (400 mL)] yielded an oily semicrystalline solid which was chromatographed [silica (40 × 2.5 cm)] with PB (1:1) as eluent. The first fraction (400 mL) was discarded and the succeeding fraction (300 mL) afforded a solid which, after recrystallization from cyclohexane, gave 1,3-diethyl-9,10-dimethyl-2,4,6,8-tetraselenaadamantane (**9**) (1.422 g, 4%) as colorless prisms, mp 159–196°C; ^{1}H NMR ($CDCl_3$) δ 1.12 (6H, t, *J* 7.2, 1, 3-*Me*CH_2), 1.33 (6H, d, *J* 6.5, 9, 10-Me), 2.03 (2H, br m, 9, 10-H), 2.04 (4H, q, *J* 7.2, 1, 3-C*H*$_2$Me), 4.19 (2H, br,m, 5, 7H); M^+ at *m/e* 482. Anal. calcd for $C_{12}H_{20}Se_4$: C, 30.02; H, 4.20. Found: C, 30.43; H, 4.52%.

Bis-(3-methyl-5-phenyl-1λ⁴,2-diselenol-1-ylium) Tetrachloroferrate(II) (**6c**). Compound (**6c**) (3.40 g, 58.7%) was obtained (procedure B) from 1-phenylbutan-1,3-dione (2.433 g) as deep green needles, mp 97–99°C. Anal. calcd for $C_{20}H_{18}Cl_4FeSe_4$: C, 31.12; H, 2.35. Found: C, 30.97; H, 2.28%.

Bis-(3-ethyl-5-phenyl-1λ⁴,2-diselenol-1-ylium) Tetrachloroferrate(II) (**6d**). Compound (**6d**) (3.40 g, 56.7%) was obtained (procedure B) from 1-phenylpentan-1,3-dione (2.64 g) as pale green crystals, mp 86–87°C. Anal. calcd for $C_{22}H_{18}Cl_4FeSe_4$: C, 33.03; H, 2.77. Found: C, 32.84; H, 2.62%.

Bis-(3-ethyl-5-p-methoxyphenyl-1λ⁴,2-diselenol-1-ylium) Tetrachloroferrate(I) (**6e**). Compound (**6e**) (4.20 g, 65.1%) was obtained (procedure B) from 1-*p*-methoxyphenylpentan-1,3-dione (3.09 g) as brown crystals, mp 104–106°C (decomposition). Anal. calcd for $C_{24}H_{26}Cl_4FeO_2Se_4$: C, 33.52; H, 3.04. Found: C, 33.41; H, 3.00%.

Bis-(3-ethyl-5,2'-thienyl-1λ⁴,2-diselenol-1-ylium) Tetrachloroferrate(I) (**6f**). Compound (**6f**) (2.41 g, 40.9%) was obtained from 1,2'-thienylpentan-1,3-dione (2.73 g) as crystals, mp 93–95°C (decomposition). The salt decomposed upon attempted recrystallization. Anal. calcd for $C_{18}H_{18}Cl_4FeS_2Se_4$: C, 26.62; H, 2.23. Found: C, 25.65; H, 2.09%.

Bis-(3-benzyl-5-phenyl-1λ⁴,2-diselenol-1-ylium) Tetrachloroferrate(II) (**6g**). Compound (**6g**) (3.00 g, 43.3%) was obtained from 1,4-diphenylbutan-1,3-dione (3.57 g) as green crystals, mp 96–98°C (decomposition). Anal. calcd for $C_{32}H_{26}Cl_4FeSe_4$: C, 41.59; H, 2.84. Found: C, 41.38; H, 2.73%.

Preparation of 1λ⁴,2-Diselenol-1-ylium Perchlorates

The following general procedures were used.

Procedure A. Perchloric acid (25.2 mL, 300 mmol) was added to a suspension of the tetrachloroferrate (**6**) (25 mmol) in acetic acid (30 mL), and the resulting mixture was warmed at 30°C with swirling until the solid became pale cream in color. The mixture was allowed to stand for 30 minutes at ambient temperature, then a large volume of ether was added to precipitate the perchlorate completely. The solid was filtered off, washed with ether, and treated as in the foregoing with a fresh portion (25.2 ml) of perchloric acid in acetic acid (30 mL). The solid was filtered off and recrystallized from acetic acid—perchloric acid (9:1, v/v). Ether was added to precipitate completely the solid, which was then filtered off, washed thoroughly with

ether to remove perchloric acid, and dried in vacuo at room temperature.

Procedure B. Perchloric acid (1 mL, 12 mmol) was added to a suspension of the tetrachloroferrate (**6**) (1 mmol) in acetic acid (2 mL), and the mixture was warmed at 30°C with swirling until the suspension became pale brown in color. The perchlorate was precipitated completely by the gradual addition of ether, filtered off and washed repeatedly with ether to ensure complete removal of perchloric acid, and dried in vacuo. Unless otherwise stated, samples for analysis were recrystallized from acetonitrile—perchloric acid (9:1, v/v), and the resulting solid was washed with ether before being dried.

3,5-Dimethyl-1λ⁴,2-diselenol-1-ylium Perchlorate (**7a**). Compound (**7a**) (81%) was obtained (procedure A) from the salt (**6a**) as cream colored crystals, mp 61–62°C; ^{1}H NMR (CF_3COOD) δ 2.88 (6H, 3, 5-Me), 8.77 (1H, 4-H). Anal. calcd for $C_5H_7ClO_4Se_2$: C, 18.51; H, 2.18. Found: C, 18.74; H, 2.26%.

3-Ethyl-4-methyl-1λ⁴,2-diselenol-1-ylium Perchlorate (**7b**). Compound (**7b**) (72%) was obtained (procedure A) from the salt (**6b**) as white plates, mp 99–100°C; ^{1}H NMR (CF_3COOD) δ 1.79 (3H, t, *J* 7.2, 3-*Me* CH_2), 2.80 (3H, 4-Me), 3.06 (2H, q, *J* 7.2, 3-MeCH_2), 11.10 (1H, 5-H). Anal. calcd for $C_6H_9ClO_4Se_2$: C, 21.29; H, 2.68; Se, 46.65. Found: C, 21.60; H, 2.85; Se, 46.70%.

3-Methyl-5-phenyl-1λ⁴,2-diselenol-1-ylium Perchlorate (**7c**). Compound (**7c**) (82%) was obtained (procedure A) from the salt (**6c**) as pale beige needles, mp 109–110°C; ^{1}H NMR (CF_3COOD) δ 2.96 (3H, 3-Me), 7.66–7.98 (5H, m, 5-Ph), 9.16 (1H, 4-H); ^{13}C NMR (CF_3COOD) δ 25.97 (3-Me), 130.73, 133.34, 137.33 (5-Ph: C-2, C-3, C-4), 138.02 (C-4), 144.83 (5-Ph: C-1), 204.69 (C-5), 205.10 (C-3). Anal. calcd for $C_{10}H_9ClO_4Se_2$: C, 31.07; H, 2.35. Found: C, 31.05; H, 2.27%.

3-Ethyl-5-phenyl-1λ⁴,2-diselenol-1-ylium Perchlorate (**7d**). Compound (**7d**) (50%) was obtained (procedure B) from the salt (**6d**) as pale beige crystals, mp 96–98°C; ^{1}H NMR (CF_3COOD) δ 1.73 (3H, t, *J* 7.4, 3-*Me*CH_2), 3.33 (2H, q, *J* 7.3, 3-MeCH_2), 7.62–8.03 (5H, m, 5-Ph), 9.17 (1H, 4-H); ^{13}C NMR (CF_3COOD) δ 16.11 (Me), 34.62 (CH_2), 130.12, 132.77, 137.41 (5-Ph: C-2, C-3, C-4), 136.97 (5-Ph: C-1), 142.36 (C-4), 203.99 (C-5), 213.00 (C-3). Anal. calcd for $C_{11}H_{11}ClO_4Se_2$: C, 32.98; H, 2.77. Found: C, 33.19; H, 2.66%.

3-Ethyl-5-p-methoxyphenyl-1λ⁴,2-diselenol-1-ylium Perchlorate (**7e**). Compound (**7e**) (100%) was obtained (procedure B) from the salt (**6e**) as reddish-brown crystals, mp 143–145°C; ^{1}H NMR (CF_3COOD) δ 1.69 (3H, t, *J* 7.4, *Me*CH_2), 3.29 (2H, q, *J* 7.4, MeCH_2), 4.04 (3H, MeO), 7.16–7.22 (2H, m, 2*m*-protons of 5-Ar), 8.03–8.06 (2H, m, 2*o*-protons of 5-Ar), 9.07 (1H, 4-H); ^{13}C NMR (CF_3COOD) δ 16.14 (Me), 34.14 (CH_2), 57.40 (MeO), 118.49 (5-Ar: C-3), 132.93 (5-Ar: C-1), 133.07 (5-Ar: C-2), 168.42 (5-Ar: C-4), 202.68 (C-5), 209.71 (C-3). Anal. calcd for $C_{12}H_{13}ClO_5Se_2$: C, 33.47; H, 3.04. Found: C, 33.25; H, 2.97%.

3-Ethyl-5,2'-thienyl-1λ⁴,2-diselenol-1-ylium Perchlorate (**7f**). Compound (**7f**) (94%) was obtained (procedure B) from the salt (**6f**) as pale brown crystals, mp 102–105°C (decomposition), which could not be recrystallized without decomposition; ^{1}H NMR (CF_3COOD) δ 1.68 (3H, t, *J* 7.4, CH_3), 3.26 (2H, q, *J* 7.4, CH_2), 7.35–7.39 (1H, m, 4'-H), 8.12–8.20 (2H, m, 3', 5'-H), 8.93 (1H, 4-H); ^{13}C NMR (CF_3COOD) δ 16.11 (Me), 33.89 (CH_2), 133.89, 137.16, 140.28, 140.86 (C-4, C-3', C-4', C-5'), 140.34 (C-2'), 192.48 (C-5), 209.47 (C-3).

3-Benzyl-5-phenyl-1λ⁴,2-diselenol-1-ylium Perchlorate (**7g**). Compound (**7g**) (97%) was obtained (procedure B) from the salt (**6g**) as pale beige crystals, mp 219–221°C (decomposition); ^{1}H NMR (CF_3COOD) δ 4.53 (2H, CH_2), 7.48–7.99 (10H, m, 2 × Ph), 9.27 (1H, 4-H); ^{13}C NMR (CF_3COOD) δ 46.58 (CH_2), 129.98, 131.05, 131.80, 132.15, 137.26, 137.70 (3-PhCH_2: C-2, C-3, C-4; 5-Ph: C-2, C-3, C-4), 137.22, 137.63 (3-PhCH_2: C-1; 5-Ph: C-1), 141.06 (C-4), 204.02 (C-5), 212.83 (C-3). Anal. calcd for $C_{11}H_{11}ClO_4Se_2$: C, 32.98; H, 2.77. Found: C, 33.19; H, 2.66%.

Reaction of 1λ⁴,2-Diselenol-1-ylium Tetrachloroferrates with Benzenediazonium Tetrafluoroborate: Formation of 6,6aλ⁴-Diselena-1,2-diazapentalenes

General Procedure. A solution of benzenediazonium tetrafluoroborate (422 mg, 2.2 mmol) in water (10 mL) was added to a suspension of the tetrachloroferrate (**6**) (1 mmol) in ethanol (120 mL). The mixture was stirred at room temperature for 40 minutes, diluted with water, and extracted with benzene. The extracts were washed with water and dried and solvent was removed and the residue chromatographed.

1,5-Diphenyl-6,6aλ⁴-diselena-1,2-diazapentalene (**10a**). The product from the salt (**6c**) was chromatographed on alumina (30 × 2.6 cm). The initial eluates [HB (3:1), 100 mL] were discarded. The succeeding purple eluates [HB (3:1), 100 mL; HB (2:1), 200 mL; B, 300 mL] were combined to give compound (**10a**) (165 mg, 21%), deep purple crystals from cyclohexane, mp 173–174°C; ^{1}H NMR ($CDCl_3$) δ 7.25–7.86 (10H, m, 1, 5-Ph), 8.48 (1H, 4-H), 8.66 (1H, 3-H); ^{13}C NMR ($CDCl_3$) δ 120.57, 126.59, 127.15, 128.19, 128.79, 129.50, 129.78, 141.57, 146.63

(1, 5-Ph + C-4), 1.38.71 (C-3), 163.41 (C-5), 175.88 (C-3a). Anal. calcd for $C_{16}H_{12}N_2Se_2$: C, 49.25, H, 3.09; N, 7.18. Found: C, 49.21; H, 2.99; N, 7.17%.

3-Methyl-1,5-diphenyl-6,6aλ^4-diselena-1,2-diazapentalene (**10b**). The product from the salt (**6d**) was chromatographed on alumina (40 × 2.6 cm). The first 100 mL of eluates (HB, 3:1) were discarded, and the succeeding purple eluates [HB (3:1), 300 mL; HB (2:1), 250 mL] yielded compound (**10b**) (331 mg, 41%), purple crystals from hexane, mp 150–151°C; ^{1}H NMR ($CDCl_3$) δ 2.77 (3H, Me), 7.27–7.83 (10H, m, 1, 5-Ph), 8.39 (1H, 4-H); ^{13}C NMR ($CDCl_3$) δ 17.89 (Me), 120.33, 126.04, 126.22, 128.20, 128.69, 129.26, 129.70, 142.60, 146.18 (1, 5-Ph + C-4), 160.78 (C-5), 176.31 (C-3a). Anal. calcd for $C_{17}H_{14}N_2Se_2$: C, 50.51; H, 3.49; N, 6.93. Found: C, 50.33; H, 3.42; N. 6.85%.

ACKNOWLEDGMENTS

We thank the Foundation for Research Development and the University of the Witwatersrand for financial support.

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