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STRUCTURE AND REACTION OF 2,6-BIS(ALKOXYCARBONYL)-1-METHYL-2*H*- AND 4*H*-SELENOPYRANIUM TETRAFLUOROBORATES

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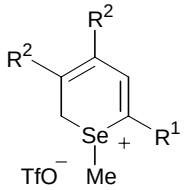
Abstract– The stereochemistry of the three isomers of 2,6-bis(ethoxycarbonyl)-1-methylselenopyranium salts was discussed on the basis of their NMR spectral data and determined to be 4*H*-, *trans*-2*H*-, and *cis*-2*H*-selenopyranium salts (**3a**, ***trans*-4a**, and ***cis*-4a**). A mixture of selenopyranium salts (**3b**) and (**4b**) reacted with carbonyl compounds at the 4-position to give 4-methylidene-4*H*-selenopyranium salts (**6**-**9**), whereas the corresponding selenabenzene (**5b**) did not react with acetone. The reaction of **5b** proceeded in the presence of BF_3·Et_2O to give selenonium salt (**6**) and demethylated product (**10**) in 65 and 33% yields, respectively.

Selenopyrylium salts have been widely studied and well documented.[1] However, only a few reports on selenopyranium salts[2] and benzoselenopyranium salts[3-5] have been published. Previously, we described the structure of monocyclic selenopyranium salts, 1-methyl-2*H*-selenopyranium trifluoromethan- sulfonates, with an electron-withdrawing group (EWG) at the 6-position,[2] which neither contained 4*H*-isomers nor isomerized to them.

Two double bonds were conjugated with the EWG. The selenopyranium salts having two EWGs at the 2- and 6-positions were expected to have the 4*H*-selenopyran structure because they form a symmetrical

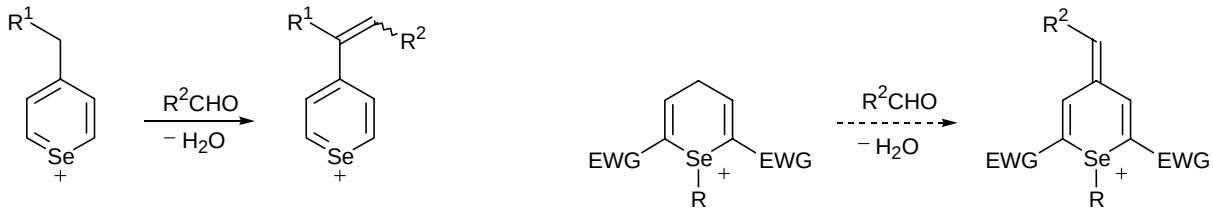


R^1=CN, R^2=Me
R^1=CN, R^2=Ph
R^1=CN, R^2=C_6H_4Cl(*p*)
R^1=COC_6H_4Br(*p*), R^2=Me
R^1=$COC_6H_4NO_2$(*p*), R^2=Me

Structures

conjugation system between a double bond and an EWG. Recently, we prepared them using the synthetic processes of selenabenzenes stabilized by two EWGs at the 2- and 6-positions.[6] Although their ^{1}H and ^{13}C NMR spectra showed the coexistence of the 2*H*- and 4*H*-isomers, we could not describe their stereostructures.

On the other hand, the selenopyrylium salts having a primary alkyl group at the 4-position are known to react with an aldehyde to afford aldol condensation products (Scheme 1)[7] because the α-methylene of the



Scheme 1

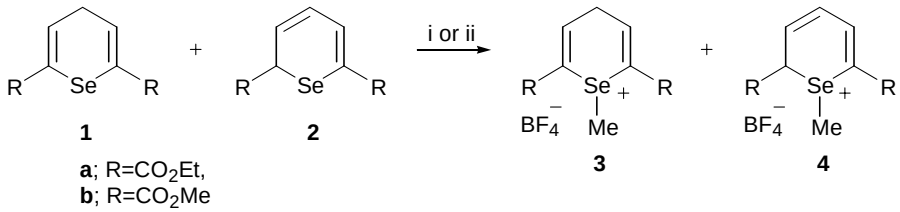
alkyl group at the 4-position is activated by the positively charged selenopyrylium ion. For this reason, it is anticipated that 4*H*-selenopyranium salts, the methylene group of which is activated by a pair of electron-withdrawing vinyl selenonio moieties, will react with an aldehyde. This paper describes the structure determination of selenopyranium salts (**3a**) and (**4a**) by NMR spectroscopy and their reactions with some carbonyl compounds.

RESULTS AND DISCUSSION

NMR SPECTROSCOPY

In the previous report, selenopyranium salts (**3**) and (**4**) were prepared by methylation of a mixture of selenopyrans (**1**) and (**2**) with iodomethane and silver tetrafluoroborate.[6] However, it was very difficult to remove the concomitant silver iodide from the mixture of **3** and **4** completely. We, therefore, used the Meerwein reagent to prepare **3** and **4** as specimens for NMR spectroscopy (Scheme 2).

^{1}H NMR spectra of the selenonium salts showed three signals of Se-methyl groups, implying that the



Scheme 2 *Reagents and conditions*: i, Me_3OBF_4 (2 equiv.), CH_2Cl_2, rt, 5 h; ii, MeI (6 equiv.), $AgBF_4$ (1.5 equiv.), CH_2Cl_2, 0 °C, 2 h.

selenonium salts consisted of three isomers. We attempted unsuccessfully to separate them. They were very unstable and decomposed during separation. Thus we used a mixture of these three isomers for NMR measurement. A mixture of ethyl esters (**3a**) and (**4a**) was more convenient to use than that of methyl esters (**3b**) and (**4b**) because the former is more soluble in $CDCl_3$ than the latter and, moreover, the H(4) signals of **3a** appeared separately from the four methylene groups of the ethoxy groups. In the case of the methyl esters, the methoxy signals of **3b** and **4b** and the H(4) signals of **3b** overlapped.

On the basis of studies on the stereochemistry of thio- and selenoxanthenium salts[8-10] and selenoxanthene selenilimines,[11] there are two possible stereoisomers for 4*H*-selenopyranium salt (**3a**), as shown in Figure 1. Conformer (**A**), whose Se-methyl group takes an equatorial position, is more stable than conformer (**B**), with an axial Se-methyl group. For 2*H*-selenopyranium salts, two diastereomers, *trans*-isomer (**C**) and *cis*-one (**D**), exist because of pyramidal inversion by reference to Mislow's[9] and our papers[4,5] on benzoselenopyranium salts.

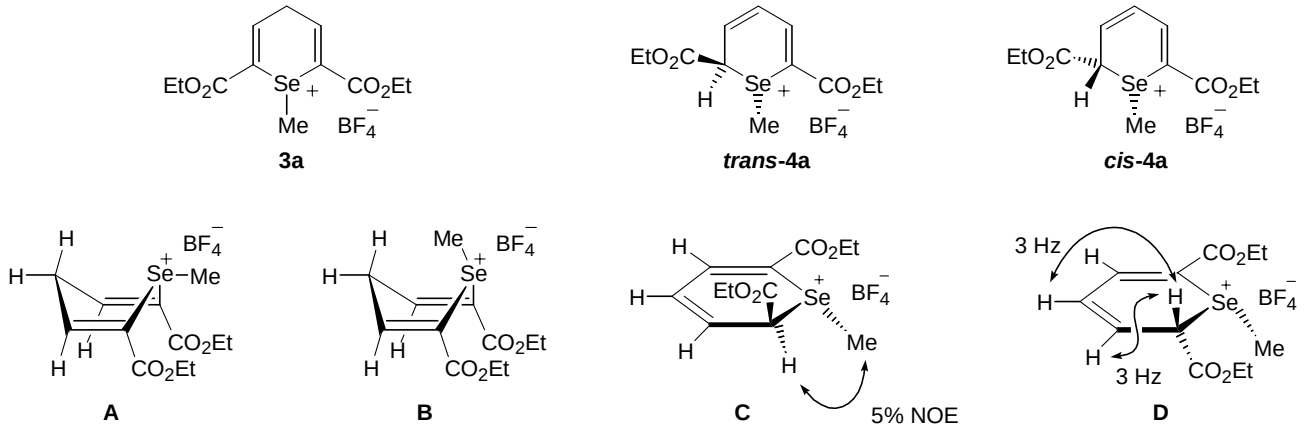


Figure 1 Stereoisomers for 4*H*- and 2*H*-selenopyranium salts

The ^{1}H NMR spectrum showed a singlet of the Se-methyl group at δ 3.09 and a pair of doublet-of-triplets due to the methylene group at δ 3.82 and 4.09 (*J*=4 and 27 Hz) as signals of 4*H*-isomer (**3a**). This observation implies that 4*H*-pyranium salt (**3a**) consists of one conformer. Decouplings of a signal due to H(3,5) at δ 7.65 changed the above-mentioned doublet-of-triplets into a pair of doublets (*J*=27 Hz). This large coupling constant is attributable to the geminal coupling between the methylene protons. Such phenomena were observed in the ^{1}H NMR spectra of 10-phenylthioxanthenium salt[10]and the corresponding selenoxanthenium salt.[12] Two protons at the 4-position of **3a** were diastereotopic because of slow ring inversion and appeared as two different signals, while the methylene protons of 4*H*-selenopyran (**1a**) appeared as a singlet. No NOE enhancement was observed between the signals of the Se-methyl group and the methylene signals. From these results, the stereostructure of **3a** was determined to be conformer (**A**).

The ^{1}H NMR spectrum of **4a** showed two sets of signals due to ***trans*-** and ***cis*-4a**, as listed in Table 1. NOE enhancement was observed between the signals of δ 2.90 due to the Se-methyl group and δ 5.57 due to the H(2), but it was not observed between the signals of δ 2.76 (Se-methyl) and 5.89 (H(2)). The former

Table 1 Analytical data of ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy ($CDCl_3$)

	3a	***trans*-4a**	***cis*-4a**
δ_H[a]	7.65 2H, t, *J* 4, 3,5-H	7.63 1H, d, *J* 7, 5-H	7.59 1H, d, *J* 7, 5-H
	4.09 1H, dt, *J* 4, 27, 4-H	6.74 1H, dd, *J* 7, 10, 4-H	6.69-6.73 1H, ddd, *J* 3, 7, 11, 4-H[b]
	3.82 1H, dt, *J* 4, 27, 4-H	6.42 1H, dd, *J* 7, 10, 3-H	6.47 1H, dd, *J* 3, 11, 3-H
		5.57 1H, d, *J* 7, 2-H	5.89 1H, t, *J* 3, 2-H
	3.09 3H, s, Se*Me*	2.90 3H, s, Se*Me*	2.76 3H, s, Se*Me*
		[4.36-4.46, m, C*H*$_2$Me	4.24-4.33, m, C*H*$_2$Me][c]
		[1.39, t, *J* 7, CH$_2$*Me*	1.29, t, *J* 7, CH$_2$*Me*][c]
δ_C	161.2 (s) C=O[d]	164.3 (s) C=O	164.6 (s) C=O
		161.5 (s) C=O	161.6 (s) C=O
	146.3 (d) 3,5-C[d]	139.0 (d) 5-C	139.4 (d) 5-C
		125.6 (d) 4-C	126.7 (d) 4-C
	119.4 (s) 2,6-C[d]	124.3 (d) 3-C	125.0 (d) 3-C
		116.9 (s) 6-C	119.2 (s) 6-C
	33.0 (t)4-C	51.7 (d) 2-C	50.1 (d) 2-C
	29.4 (q) Se*Me*	19.4 (q) Se*Me*	15.9 (q) Se*Me*
	64.1 (t)*C*H$_2$Me[d]	64.5 (t)*C*H$_2$Me	65.0 (t)*C*H$_2$Me
		64.0 (t)*C*H$_2$Me	63.8 (t)*C*H$_2$Me
	[13.7 (q) CH$_2$*Me*	13.8 (q) CH$_2$*Me*	13.6 (q) CH$_2$*Me*][c]
δ_{Se}	268	277	276

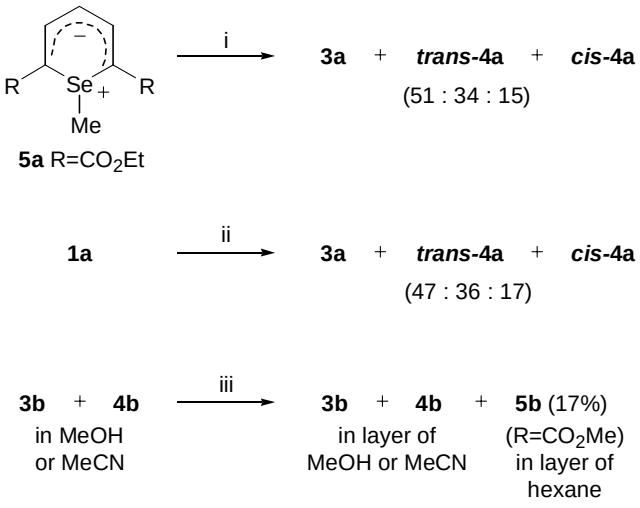
[a] *J* (Hz), [b]The signal overlapped with a signal at δ 6.73 of ***trans*-4a**. Therefore, its coupling constants were deteremined by irradiation of the signals at δ 5.89, 7.59, and 6.47. [c]These signals could not be precisely assigned. [d]This denotes two overlapping signals.

compound was designated ***trans*-4a** and the latter ***cis*-4a**. Proton decoupling of the H(2)-methine signal at δ 5.89 of ***cis*-4a** changed a doublet-of-doublet signal (*J*=3 and 11 Hz) of H(3) and a doublet-of-doublet-of-doublet (*J*=3, 7 and 11 Hz) of H(4) into a doublet (*J*=11 Hz) and a doublet-of-doublet (*J*=7 and 11 Hz), respectively. The allylic coupling (*J*=3 Hz) between H(2) and H(4) was found from the change in the H(4) signal.

The carbon signals of Se-methyl groups of **3a**, ***trans*-4a**, and ***cis*-4a** and C(2), C(3), and C(4) of ***trans*-4a** and ***cis*-4a** were assigned by an H,C-correlation spectroscopy (COSY) spectrum showing the following correlations: δ_H(SeMe) 3.09 and δ_C 29.4 for **3a**; δ_H(SeMe) 2.90 and δ_C 19.4, δ_H(2) 5.57 and δ_C 51.7, δ_H(3) 6.42 and δ_C 124.3, δ_H(4) 6.74 and δ_C 125.6, δ_H(5) 7.63 and δ_C 139.0 for ***trans*-4a**; δ_H(SeMe) 2.76 and δ_C 15.9, δ_H(2) 5.89 and δ_C 50.1, δ_H(3) 6.47 and δ_C 125.0, δ_H(4) 6.69-6.73 and δ_C 126.7, δ_H(5) 7.59 and δ_C 139.4 for ***cis*-4a**.

The isomer ratio was **3a** : ***trans*-4a** : ***cis*-4a** = 47 : 36 : 17 from the intensities of their Se-methyl groups in the ^{1}H NMR spectrum. On the other hand, selenabenzene (**5a**) was protonated with tetrafluoroboric acid to give a mixture of **3a**, ***trans*-4a**, and ***cis*-4a** (51 : 34 : 15) (Scheme 3). These two isomer ratios were very close. The low ratio of ***cis*-4a** is attributable to steric hinderance between the Se-methyl and the ethoxycarbonyl groups at the 2-position.

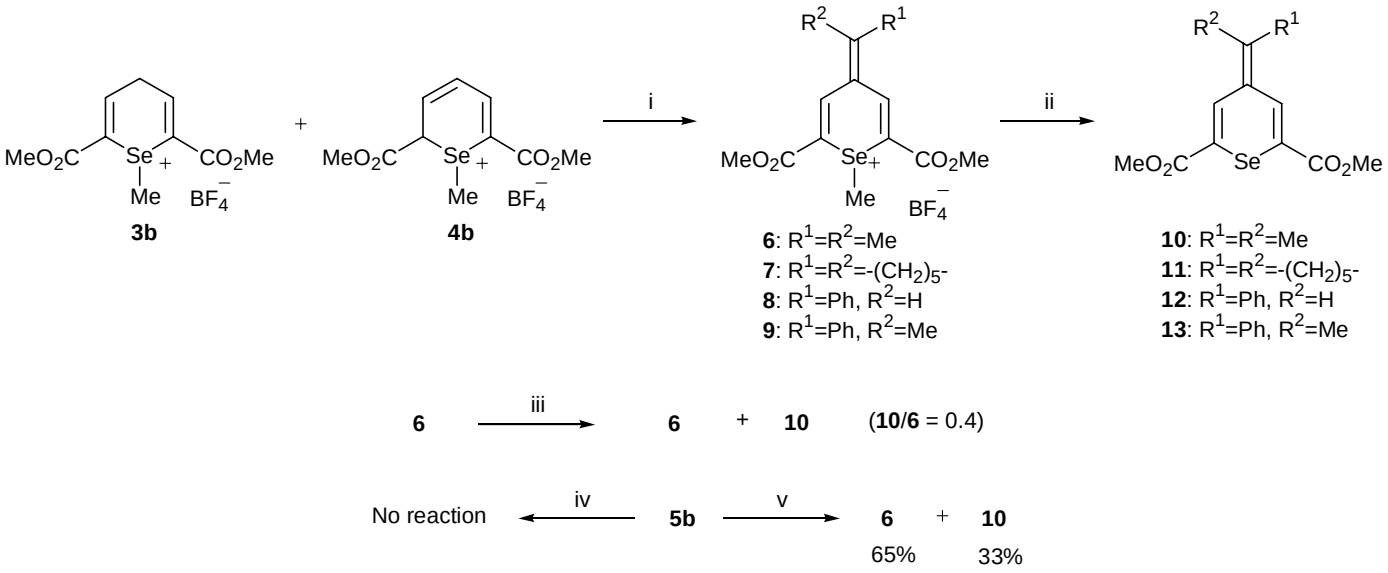
Interestingly, on washing a mixture of **3b** and **4b** in methanol or acetonitrile with hexane three times, selenabenzene (**5b**), produced in solution by deprotonation at the 4-position of **3b** and 2-position of **4b**, was isolated in 17% yield from the hexane layer (Scheme 3). This evidence shows that these protons have high acidity and are deprotonated easily.



Scheme 3 *Reagents and conditions*: i, HBF_4 in H_2O (1 equiv.), EtOH, 0 °C, 5 h; ii, Me_3OBF_4 (2 equiv.), CH_2Cl_2, rt, 5 h; iii, shaking with hexane.

REACTIONS WITH CARBONYL COMPOUNDS

Reactions of a mixture of 4*H*- and 2*H*-selenopyranium salts (**3b**) and (**4b**) in dichloromethane with carbonyl compounds were conducted at 0 °C for 2 hours to produce 4-methylidene-4*H*-selenopyranium salts (**6-9**) in good yields (Scheme 4). Compounds (**6-9**) gave satisfactory ^{1}H and ^{13}C NMR, IR, and MS spectroscopic



Scheme 4 *Reagents and conditions*: i, R^1COR^2 (5 equiv.), EtOH, 0 °C, 2 h; ii, KBr (1.2 equiv.), EtOH,0 °C, 5 min; iii, 170 °C, 10 sec, neat; iv, acetone (excess), rt, overnight; v, acetone (5 equiv.), $BF_3{\cdot}Et_2O$ (1 equiv.), CH_2Cl_2, 0 °C, 1 h.

analysis. Down-field-shifted signals in ^{13}C NMR spectra of **6-9** were observed at δ 158.6-181.4. These characteristic signals were assigned to the exo-methylene carbon C(1') at the 4-position because the selenonio group abstracts the electrons of the double bonds and the exo-methylene carbon is electron-deficient. This was confirmed by comparing the ^{13}C NMR spectra of selenonium salts (**6**) and (**8**) with those of 4-methylideneselenopyrans (**10**) and (**12**), respectively. Compound (**10**) or (**12**) was prepared by demethylation of **6** or **8** with potassium bromide, respectively. The ^{13}C NMR signals of **6**, **8**, **10**, and **12** are listed in Table 2.

The C(1') signal at δ 158.6 of **8** was shifted to that at δ 135.2 of **12**. A similar up-field shift was observed between the C(1') carbons of **6** (δ 173.8) and **10** (δ 140.3). Four signals of quaternary carbons C(2), C(4), C(6), and C(Ar^{ipso}) of **12** could not be assigned. Three olefinic protons of **8** and **12** were detected by NOE enhancement (Figure 2), and olefinic carbons were assigned based on their C-H correlations in H,C COSY spectra: δ_H(1') 8.00 and δ_C 158.6, δ_H(5) 8.06 and δ_C 146.3, δ_H(3) 8.22 and δ_C 140.2 for **8**; δ_H(1') 6.74 and δ_C 135.2, δ_H(5) 7.56 and δ_C 137.9, δ_H(3) 8.07 and δ_C 131.4 for **12**.

Table 2 Selected ^{13}C NMR data for **6**, **10**, **8**, and **12**.

6 ($CDCl_3$)		**10** ($CDCl_3$)		**8** (CD_3CN)		**12** ($CDCl_3$)	
δ_C	113.8 (s)	δ_C	121.3 (s)	δ_C	117.6 (s)	δ_C	123.7 (s)
δ_C	124.6 (s)	δ_C	127.6 (s)	δ_C	120.3 (s)	δ_C	126.9 (s)
δ_C (3,5)	140.6 (d)	δ_C (3,5)	132.8 (d)	δ_C	128.3 (s)	δ_C (3)	131.4 (d)
δ_C (1')	173.8 (s)	δ_C (1')	140.3 (s)	δ_C	134.8 (s)	δ_C	132.7 (s)
				δ_C (3)	140.2 (d)	δ_C (1')	135.2 (d)
				δ_C (5)	146.3 (d)	δ_C	136.2 (s)
				δ_C (1')	158.6 (d)	δ_C (5)	137.9 (d)

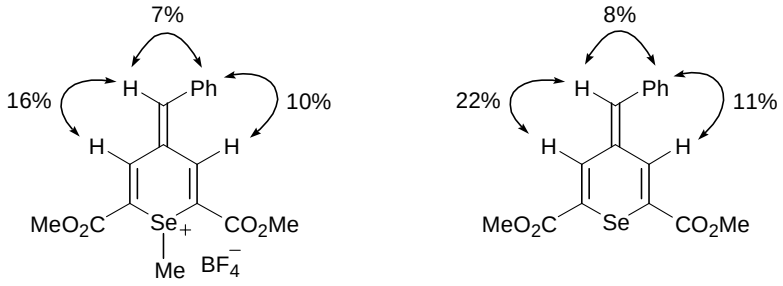
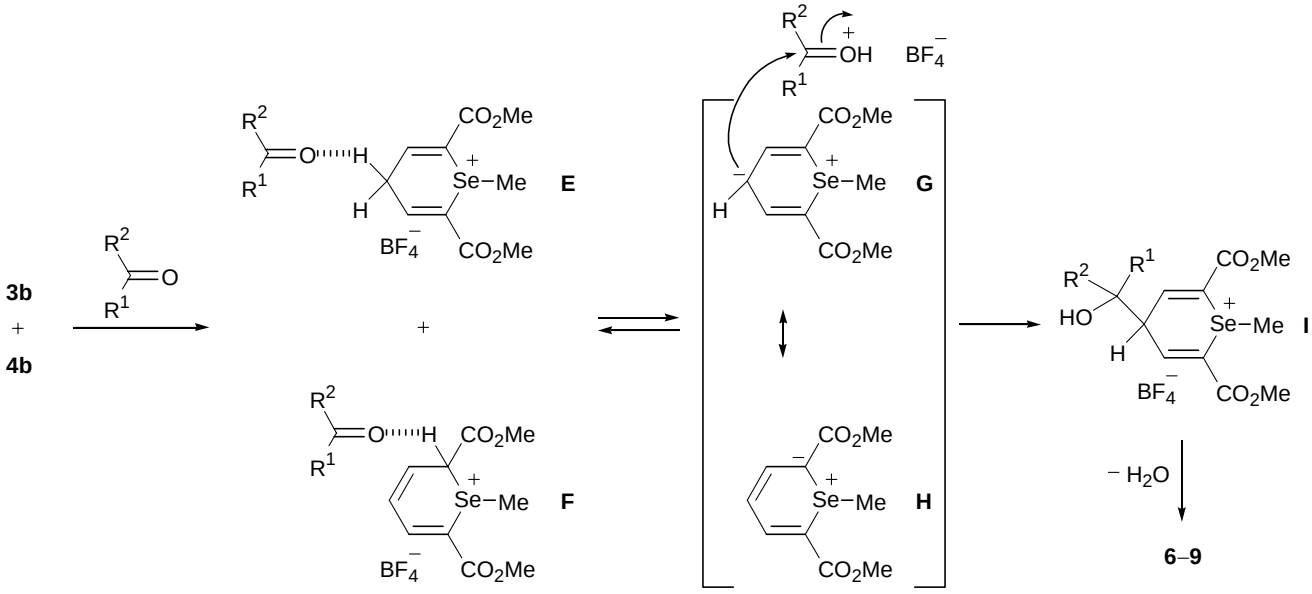


Figure 2 NOE enhancement in ^1H NMR spectra of **8** and **12**



Scheme 5

The reaction mechanism for the formation of **6-9** is shown in Scheme 5. First, deprotonation of H(4) of **3b** and H(2) of **4b** was accelerated by their interaction with the oxygen atom of a carbonyl compound, such as **E** and **F**, respectively. The resulting selenabenzene intermediates (**G**) and (**H**) reacted with carbonyl compounds activated by protonation to give alcohol (**I**). Dehydration of the alcohol (**I**) afforded 4-methylidene-4*H*-selenopyranium salts (**6**-**9**).

When the salt (**6**) was heated at its melting point for 10 seconds in the solid phase, a mixture of **6** and demethylated product (**10**) (**10**/**6**=0.4) was obtained. Although selenabenzene (**5b**) did not react with acetone, it reacted with acetone in the presence of boron trifluoride etherate to give salt (**6**) (65%) and selenopyran (**10**) (33%). The acid would assist in the formation of selenonium salt (**I**) or the dehydration of **I**.

CONCLUSION

Methylation of 4*H*- and 2*H*-selenopyrans (**1a**) and (**2a**) afforded three isomers of Se-methyl selenonium salts (**A**), (**C**), and (**D**) in a ratio of 47 : 36 : 17. Treatment of selenabenzene (**5a**) with tetrafluoroboric acid gave the same products in almost the same ratio. A mixture of 4*H*- and 2*H*-selenopyranium salts (**3b**) and (**4b**) reacted as active methylene compounds with ketones or benzaldehyde at the 4-position to give 4-methylidene-4*H*-selenopyranium salts (**6**-**9**).

EXPERIMENTAL

Melting points were obtained with a Yanagimoto micro-melting-point apparatus and are uncorrected. IR spectra of solids (KBr) and liquids (NaCl) were recorded on a JASCO FT/IR-230 spectrophotometer. The ^{1}H, ^{13}C, and ^{77}Se NMR spectra were measured at 400, 100, and 76 MHz, respectively, with a JEOL EX-400 spectrometer. The ^{1}H, ^{13}C, and ^{77}Se chemical shifts are given in ppm relative to those of internal tetramethylsilane, $CDCl_3$ or CD_3CN as solvent, and external dimethyl selenide, respectively. The *J* values are given in Hz. MS spectra were recorded on a JEOL JMS-SX 102A spectrometer with a direct-insertion probe at 70 eV. Elemental analyses of new compounds were performed by a Yanaco CHN Corder MT-5. All chromatographic isolations were accomplished with either Kieselgel 60 (Merck) or BW-127ZH (Fuji Silysia) for column chromatography or Kieselgel 60 PF254 containing gypsum (Merck) for PTLC.

Synthesis of 2,6-bis(ethoxycarbonyl)-1-methyl-2*H*- and 4*H*-selenopyranium tetrafluoroborates (3a, 4a)

To a mixture of diethyl 2*H*- and 4*H*-selenopyran-2,6-dicarboxylates (**1a**) and (**2a**) (10:1) (200 mg, 0.69

mmol) in dichloromethane (7 mL) was added trimethyloxonium tetrafluoroborate (306 mg, 1.4 mmol). The whole was stirred for 5 h at rt. The excess trimethyloxonium tetrafluoroborate was filtered off and washed with dichloromethane. The filtrate and the washings were combined and concentrated to dryness. The residue was washed with ether several times and dried under reduced pressure to give a mixture of 2,6-bis(ethoxycarbonyl)-1-methyl-2*H*- and 4*H*-selenopyranium tetrafluoroborate (**3a**, **4a**) (270 mg, quant.), dark red oil; ν_{max}(film)/cm^{-1} 1732 (ester C=O). Data for ^{1}H, ^{13}C, and ^{77}Se NMR are shown in Table 1.

Synthesis of 2,6-bis(methoxycarbonyl)-4-isopropylidene-1-methyl-4*H*-selenopyranium tetrafluoroborate (6)

A mixture of 2,6-bis(methoxycarbonyl)-1-methyl-2*H*- and 4*H*-selenopyranium tetrafluoroborates (**3b**) and (**4b**) was prepared from dimethyl 4*H*-selenopyran-2,6-dicarboxylate (**1b**) (261 mg, 1 mmol), iodomethane (0.4 mL, 6 mmol), and silver tetrafluoroborate (324 mg, 1.5 mmol). [6] A mixture of **3b**, **4b**, and acetone (0.37 mL, 5 mmol) in ethanol (15 mL) was stirred for 2 h at 0 °C. The solvent was removed under reduced pressure. The resulting crystals were filtered and recrystallized from dichloromethane to afford pale yellow plates (302 mg, 75%), mp 170 °C (decomp) (from dichloromethane); ν_{max}(KBr)/cm^{-1} 1700 (ester C=O), 1040 (BF_4^-); ^{1}H NMR (400 MHz; $CDCl_3$): δ 2.43 (6 H, s, =CC*H*$_3$ × 2), 3.15 (3 H, s, SeMe), 4.02 (6 H, s, OMe × 2), 8.28 (2 H, s, 3- and 5-H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 24.3 (q × 2), 31.4 (q), 54.5 (q × 2), 113.8 (s × 2), 124.6 (s), 140.6 (d × 2), 163.0 (s × 2), 173.8 (s); ^{77}Se NMR (76 MHz; $CDCl_3$): δ 287; *m/z* (EI) 302 (M^+–$MeBF_4$, 88%), 287 (100). *Anal*. Calcd for $C_{13}H_{17}O_4BF_4Se$: C, 38.74; H, 4.25. Found: C, 38.63;H, 4.18.

2,6-Bis(methoxycarbonyl)-4-cyclohexylidene-1-methyl-4*H*-selenopyranium tetrafluoroborate (7)

This compound was similarly prepared from **3b**, **4b**, and cyclohexanone (491 mg, 5 mmol).

Brown oil (257 mg, 58%); ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.72-1.90 (6 H, m, 3'-, 4'- and 5'-H), 2.80 (4 H, t, *J*=5 Hz, 2'- and 6'-H), 3.11 (3 H, s, SeMe), 4.01 (6 H, s, OMe × 2), 8.34 (2 H, s, 3- and 5-H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 25.9 (t), 29.2 (t × 2), 31.3 (q), 34.0 (t × 2), 54.4 (q × 2), 114.5 (s × 2), 121.4 (s), 139.8 (d × 2), 163.0 (s × 2), 181.4 (s); ^{77}Se NMR (76 MHz; $CDCl_3$): δ 290.

This compound was so unstable at room temperature that a small amount of an unidentified contaminant could not be removed. Therefore, these peaks were picked up from the ^{1}H and ^{13}C NMR spectra of the mixture.

2,6-Bis(methoxycarbonyl)-4-benzylidene-1-methyl-4*H*-selenopyraniumtetrafluoroborate(8)

This compound was similarly prepared from **3b**, **4b**, and benzaldehyde (1 mL, 10 mmol).

Yellow needles (271 mg, 60%), mp 169-170 °C (decomp) (from acetonitrile-hexane); ν_{max}(KBr)/cm^{-1} 1690 (ester C=O), 1040 (BF_4^-); ^{1}H NMR (400 MHz; CD_3CN): δ 3.08 (3 H, s, SeMe), 3.95 (3 H, s, OMe), 3.99 (3 H, s, OMe), 7.57-7.60 (5 H, m, aromatic), 8.00 (1 H, s, 1'-H), 8.06 (1 H, s, 5-H), 8.22 (1 H, s, 3-H). The 3- and 5-H signals were determined by the NOE experiment. ^{13}C NMR (100 MHz; CD_3CN): δ 32.0 (q), 55.1 (q), 55.2 (q), 117.6 (s), 120.3 (s), 128.3 (s), 130.4 (d × 2), 131.9 (d × 2), 133.2 (d), 134.8 (s), 140.2 (d), 146.3 (d), 158.6 (d), 163.2 (s), 163.3 (s); ^{77}Se NMR (76 MHz; CD_3CN): δ 314; *m/z* (EI) 350 (M^+–$MeBF_4$, 100%). *Anal*. Calcd for $C_{17}H_{17}O_4BF_4Se$: C, 45.27; H, 3.80. Found: C, 45.25; H, 3.74.

2,6-Bis(methoxycarbonyl)-4-(1-phenylethylidene)-1-methyl-4*H*-selenopyranium tetrafluoroborate (9)

This compound was similarly prepared from **3b**, **4b**, and acetophenone (601 mg, 5 mmol).

Light brown powder (372 mg, 80%), mp 152-153 °C (decomp) (from dichloromethane); ν_{max}(film)/cm^{-1} 1705 (ester C=O), 1038 (BF_4^-); ^{1}H NMR (400 MHz; $CDCl_3$): δ 2.68 (3 H, s, =C(Ph)C*H*$_3$), 3.14 (3 H, s, SeMe), 3.86 (3 H, s, OMe), 4.02 (3 H, s, OMe), 7.37-7.50 (5 H, m, aromatic), 7.85 (1 H, s, 5-H), 8.38 (1 H, s, 3-H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 24.0 (q), 31.1 (q), 54.3 (q), 54.4 (q), 114.1 (s),116.3 (s), 125.2 (s), 128.6 (d × 2), 128.9 (d × 2), 130.8 (d), 139.5 (s), 140.6 (d), 142.6 (d), 162.66 (s), 162.73 (s), 171.4 (s); ^{77}Se NMR (76 MHz; $CDCl_3$): δ 296; *m/z* (EI) 364 (M^+-$MeBF_4$, 100%).

Dimethyl 4-isopropylidene-4*H*-selenopyran-2,6-dicarboxylate (10)

Potassium bromide (71 mg, 0.6 mmol) was added to a solution of 2,6-bis(methoxycarbonyl)-4-isopropylidene-1-methyl-4*H*-selenopyranium tetrafluoroborate (**6**) (202 mg, 0.5 mmol) in ethanol (5 mL). The mixture was stirred for 5 min at 0 °C, and water and ether were added to it. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined, dried ($MgSO_4$), and concentrated to dryness. The residue was purified by PTLC using hexane-AcOEt (2:1) to give 4-isopropylidene-4*H*-selenopyran-2,6-dicarboxylate (**10**) (8 mg, 5%), yellow needles, mp 167-168 °C (from ether-hexane); ν_{max}(film)/cm^{-1} 1700 (ester C=O); ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.89 (6 H, s, =CC*H*$_3$ × 2), 3.84 (6 H, s, OMe × 2), 7.74 (2 H, s, 3- and 5-H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 21.9 (q × 2), 52.7 (q × 2), 121.3 (s × 2), 127.6 (s), 132.8 (d × 2), 140.3 (s), 165.1 (s × 2); ^{77}Se NMR (76 MHz; $CDCl_3$): δ 302; *m/z* (EI) 302 (M^+, 75%), 287 (100). HRMS calcd for $C_{12}H_{14}O_4Se$: 302.0058. Found: 302.0042.

Dimethyl 4-cyclohexylidene-4*H*-selenopyran-2,6-dicarboxylate (11)

This compound was similarly prepared from **7** (222 mg, 0.5 mmol).

Yellow oil (7 mg, 4%); ν_{max}(film)/cm^{-1} 1706 (ester C=O); ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.56 (4 H, br s, aliphatic), 1.63 (3 H, br s, aliphatic), 2.37 (3 H, br s, aliphatic), 3.84 (6 H, s, OMe), 7.83 (2 H, s, 3-and 5-H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 26.6 (t), 28.2 (t × 2), 31.6 (t × 2), 52.7 (q × 2), 121.9 (s × 2), 124.7 (s), 132.6 (d × 2), 149.4 (s), 165.2 (s × 2); ^{77}Se NMR (76 MHz; $CDCl_3$): δ 455; *m/z* (EI) 342 (M^+, 100%). HRMS calcd for $C_{15}H_{18}O_4Se$: 342.0370. Found: 342.0361.

Dimethyl 4-benzylidene-4*H*-selenopyran-2,6-dicarboxylate (12)

This compound was similarly prepared from **8** (226 mg, 0.5 mmol).

Yellow needles (111 mg, 63%), mp 152-153 °C (decomp) (from chloroform); ν_{max}(KBr)/cm^{-1} 1690 (ester C=O); ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.84 (3 H, s, OMe), 3.87 (3 H, s, OMe), 6.74 (1 H, s, 1'-H), 7.31-7.38 (5 H, m, aromatic), 7.56 (1 H, s, 5-H), 8.07 (1 H, s, 3-H). The 3- and 5-H signals were determined by the NOE experiment. ^{13}C NMR (100 MHz; $CDCl_3$): δ 52.8 (q), 52.9 (q), 123.7 (s), 126.9 (s), 128.2 (d), 128.4 (d × 2), 128.7 (d × 2), 131.4 (d), 132.7 (s), 135.2 (d), 136.2 (s), 137.9 (d), 164.5 (s), 164.6 (s); ^{77}Se NMR (76 MHz; $CDCl_3$): δ 344; *m/z* (EI) 350 (M^+, 100%). *Anal*. Calcd for $C_{16}H_{14}O_4Se$: C, 55.03; H, 4.04. Found: C, 54.75; H, 4.00.

Dimethyl 4-(1-phenylethylidene)-4*H*-selenopyran-2,6-dicarboxylate (13)

This compound was similarly prepared from **9** (233 mg, 0.5 mmol).

Yellow powder (16 mg, 9%), mp 92-93 °C (from chloroform); ν_{max}(film)/cm^{-1} 1704 (ester C=O); ^{1}H NMR (400 MHz; $CDCl_3$): δ 2.17 (3 H, s, Me), 3.73 (3 H, s, OMe), 3.88 (3 H, s, OMe), 7.20-7.22 (2 H, m, aromatic), 7.32-7.40 (3 H, m, aromatic), 7.59 (1 H, s, 3-H), 7.88 (1 H, d, *J*=1 Hz, 5-H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 21.8 (q), 52.7 (q), 52.9 (q), 121.7 (s), 124.5 (s), 127.8 (d · 2), 127.9 (d), 128.6 (d · 2), 128.9 (s), 132.6 (d), 134.4 (d), 142.3 (s), 142.5 (s), 164.8 (s), 164.9 (s); ^{77}Se NMR (76 MHz; $CDCl_3$): δ 320; *m/z* (EI) 364 (M^+, 100%). HRMS calcd for $C_{15}H_{18}O_4Se$: 364.0214. Found: 364.0205.

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