Syntheses and Properties of Selenium-bridged Bischromones

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The preparation of the new selenium-bridged chromones **5a-e** is described. Compound **5c** reacts with *m*-CPBA under various conditions to give the corresponding selenoxide **7** and the Pummerer products **8** and **9**. The selenides **5a-c** react with excess *m*-CPBA to form the diselenides **13a-c**. Oxidation of **13c** with hydrogen peroxide afforded the chromone-3-seleninic acid **22**.

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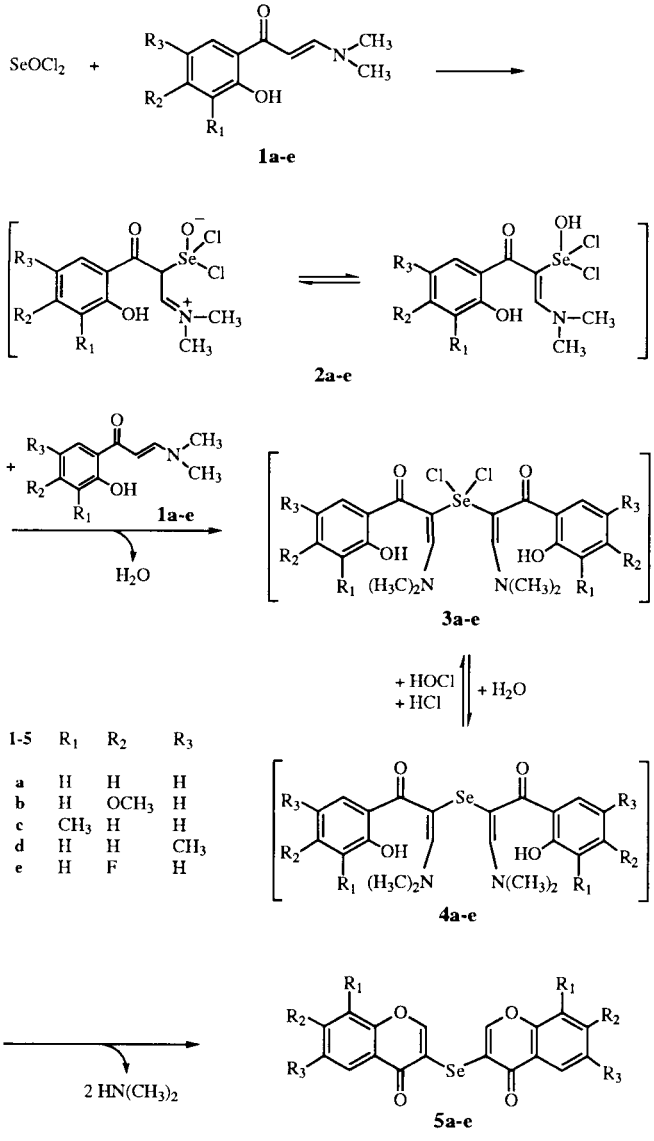
Selenium oxychloride reacts with enaminones of the 2-hydroxyphenylethanone type to form selenium-bridged bischromones. The reaction sequence begins with electrophilic addition of a selenium oxychloride molecule to the electron-rich α-carbon atom at the carbonyl site of the enaminone **1a** [1], **1b,d** [2], **1c,e** [3], thus forming the intermediates **2a-e**. The intermediates **2a-e** react with a second enaminone, thereby eliminating water to form the still open-ringed selenodichloro products **3a-e**. The reaction water subsequently hydrolyses the selenodichloro group, resulting in the open-ringed selenides **4a-e** and chlorine, whereby the latter disproportionates into hypochlorite and hydrogen chloride. Hydrogen chloride promotes ring closure and thus the formation of the bischromones **5a-e**. This occurs *via* the elimination of two moles of dimethylamine (Scheme I).

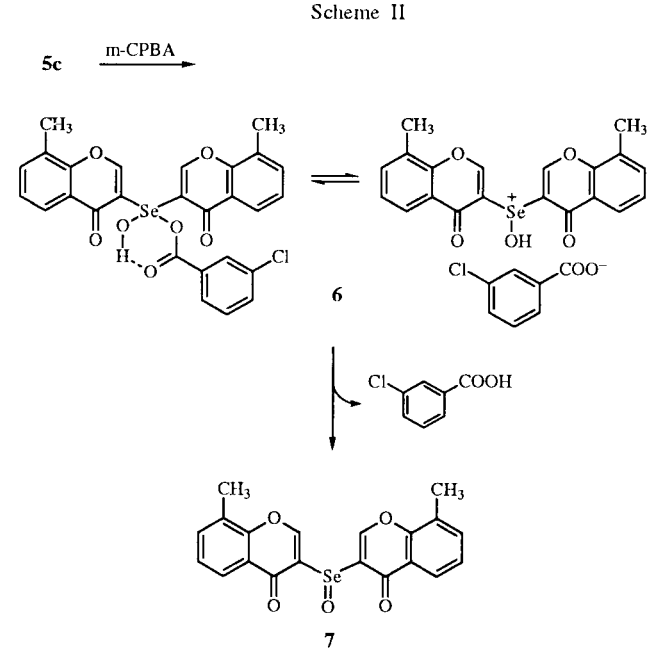
In order to initiate the formation of a bischromonyl selenoxide, the selenide **5c** is oxidized in chloroform in the presence of *m*-chloroperbenzoic acid (*m*-CPBA) in tetrachloromethane. When cooled, compound **6** forms as a precipitate. In **6**, the selenium atom a) has been oxidized and at the same time has a molecule of *m*-chlorobenzoic acid attached, or b) it exists as an ion pair. Dissolving **6** in boiling acetone releases *m*-chlorobenzoic acid, and the bischromonyl selenoxide **7** precipitates in the still hot solvent (Scheme II).

Scheme I



1-5	R_1	R_2	R_3
a	H	H	H
b	H	OCH_3	H
c	CH_3	H	H
d	H	H	CH_3
e	H	F	H

Scheme II



In contrast, if the bischromone **5c** is oxidized with equimolar *m*-CPBA exclusively in chloroform, the Pummerer product **8** develops as a precipitate when the chloroform solution is evaporated to dryness and the residue is subsequently dissolved in ethanol and cooled for several days. Compound **8** develops when one chromone structure is transformed into an ethoxy- and chlorobenzoate-substituted chromanone. Even though this substitution pattern occurs preferentially, we only once were able to isolate the analogue Pummerer product **9**. The compound **9** has an ethoxy group at positions 2 and 3 (Figure 1).

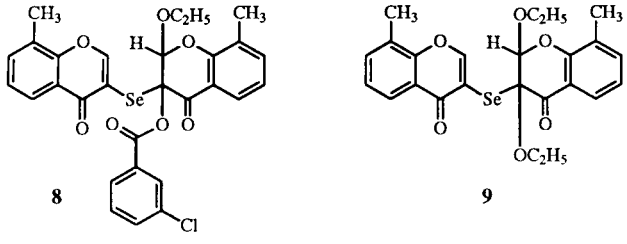


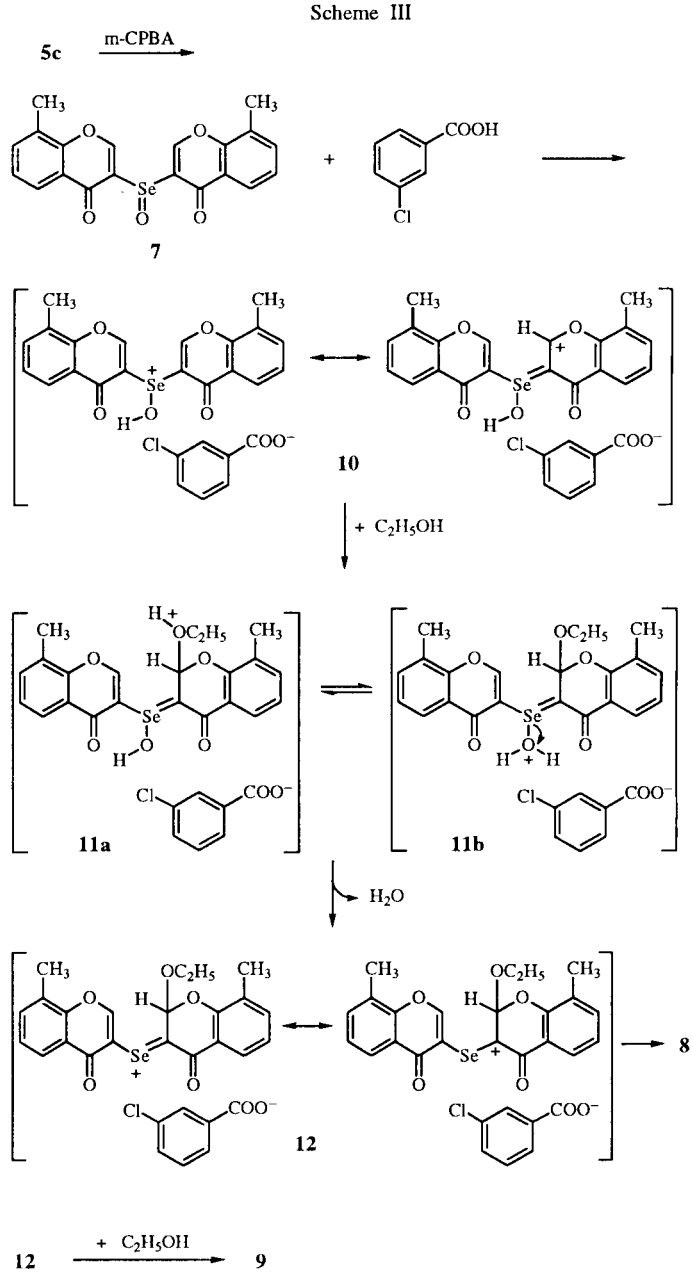
Figure 1

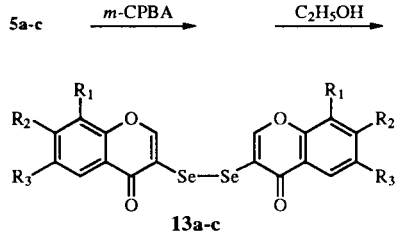
The structures of **8** and **9** were confirmed by ^{1}H nmr spectroscopy. In **8**, the H-2 singlet of the chromone is found at 8.58 ppm, whereas the corresponding proton of **9** occurs at 8.42 ppm. The acetalic hydrogen atoms of the partial chromanone structures occur at 6.06 ppm in **8** and at 5.54 ppm in **9**. An interesting feature of the ^{1}H nmr spectrum of each of the compounds is the pattern of the diastereotopic methylene protons within the ethoxy groups. Accordingly, the methylene protons of both the ethoxy groups of **9** occur as a multiplet occuring between 3.65 and 4.02 ppm. The methylene protons of the ethoxy substituents of **8** are also found as a multiplet in the ^{1}H nmr spectrum between 3.91 and 4.12 ppm.

The formation of these products is suggestive of an underlying Pummerer reaction mechanism. However, the selenoxide **7** has no α-hydrogen atom beside the selenoxide group. Therefore, an Additive Seleno-Pummerer reaction has been suggested in explanation of the formation of **8** and **9** (Scheme III). Although no such reactions have heretofore been carried out with selenoxides, some have been performed with sulfoxides [4,5]. Before this reaction can take place, the selenoxide **7** must arise *in situ* during oxidation of the seleno-bischromone **5c** in chloroform. The selenoxide group is then protonated by 3-chlorobenzoic acid, during the course of which the type **10** compounds are formed. In these compounds, the positive charge can be delocalized to the C-2 atom. One mole of ethanol then attaches to the thereby formed carbenium ion. The resulting oxonium compound **11a** is in equilibrium with the product **11b**, which in turn gives the intermediate **12** after dehydration. The intermediate **12** has an selenium-carbenium structural element. The electron-poor C-3 atom in **12**'s chromanone ring now provides the means for a further nucleophilic attack, which can be initiated from another ethanol molecule or from a competing benzoate anion. The Pummerer products **8** and **9** are the end products of this reaction sequence.

When the seleno-bischromones **5a-c** are oxidized in excess *m*-CPBA in chloroform, the diseleno-bischromones **13a-c** form as a precipitate after the mixture has been evaporated to dryness and the residue is treated with ethanol (Figure 2). A potential pathway for the formation of these diselenides is as follows: Due to the hydrolysis resulting from the selenium-carbenium structure of the

Scheme III





13a-c

13	R_1	R_2	R_3
a	H	H	H
b	H	OCH_3	H
c	CH_3	H	H

Figure 2

intermediate **12**, derived from **5c**, chromone selenol **14** by way of example develops and subsequently becomes oxidized to form the diseleno-bischromone **13c** [6]. The 2-ethoxy-3-hydroxychromone **15** forms as a byproduct of the reaction (Figure 3). We were able to provide proof of this by isolation of compound **15** from the ethanol filtrate

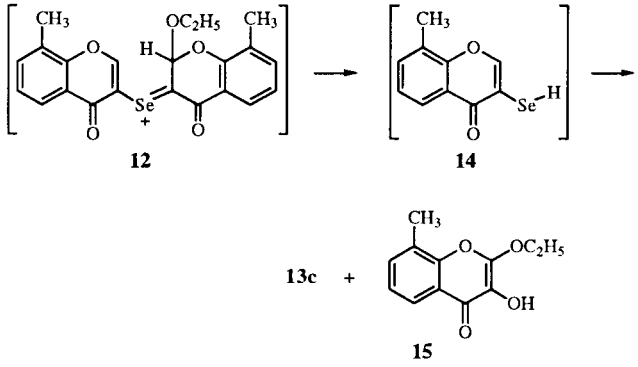
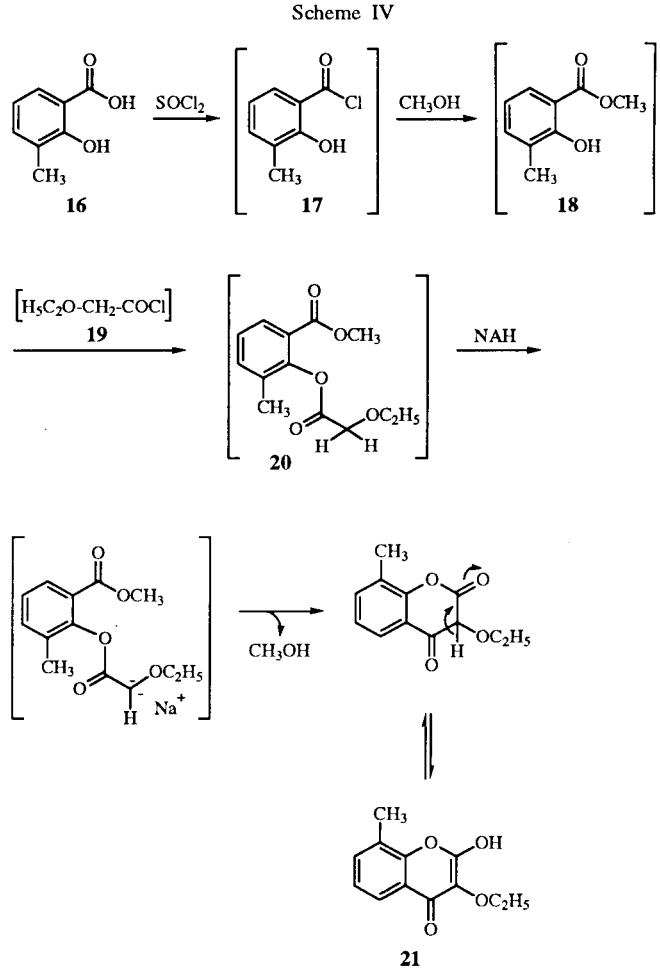


Figure 3

by means of preparative thin layer chromatography. In order to have unequivocal structural identification, the compound 2-hydroxy-3-ethoxychromone **21**, which is structurally isomeric to **15**, was also prepared by a different method. This was done by causing the 2-hydroxy-3-methylbenzoic acid chloride **17** to react with methanol to form the methyl ester **18**. With ethoxyacetic acid's acid chloride **19** [7], the 2-hydroxy group of **18** reacts in such a way to give the diester **20**. Ring closure giving the product **21** took place *via* an intramolecular Claisen reaction with sodium hydride (Scheme IV). One can differentiate well between the thus prepared compounds **15** and **21** by causing them to react with Fe(III)-ions. Whereas **15** develops a strong, blue color with Fe(III)-chloride, **21** does not form any complexes with it [8].

Fission of diseleno-bischromones can be caused by using a 35 percent hydrogen peroxide solution in dioxane [9]. Compound **13c**'s yellow coloring, attributable to Se-

Scheme IV



Se-chromophore, disappears during the course of the reaction. After the addition of water, a high yield of the chromone seleninic acid **22** forms as a precipitate (Figure 4).

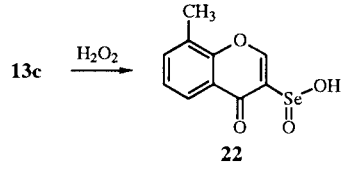


Figure 4

EXPERIMENTAL

General Methods.

Melting points were determined on a Linström apparatus and are uncorrected. The ir spectra were recorded on a Perkin-Elmer 297 spectrometer. The ^1H nmr specta were recorded on a Bruker AC 300 spectrometer. Mass spectra were obtained on a Finnegan MAT Bremen CH-7A spectrometer and Finnigan MAT Bremen

CH-5 DF. Elemental analyses were performed by the Institut für Pharmazie Analytical Service Laboratory.

General Procedure for the Preparation of **5a-e**.

A solution of selenium oxychloride (265 mg, 1.6 mmoles) in dry toluene (5 ml) was added dropwise to a vigorously stirred solution of **1a** (500 mg, 2.6 mmoles), **1b** (500 mg, 2.26 mmoles), **1c** (500 mg, 2.4 mmoles), **1d** (500 mg, 2.4 mmoles) and **1e** (500 mg, 2.39 mmoles) in toluene (40 ml) in the presence of traces (2 drops) of water. The green colored solution became colorless and the resulting conpounds were filtered and recrystallized from ethanol to give colorless crystals.

3, 3'-Selenobis-(4*H*-[1]-benzopyran-4-one) (**5a**).

The yield was 312 mg (64%), mp 195°; ir 3428, 3054, 1630, 1609, 1550, 1460, 1344, 1309, 1110, 1070, 875, 757, 692 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 7.54 (t, 2H, J = 7 Hz, H-7, H-7'), 7.68 (d, 2H, J = 8 Hz, H-8, H-8'), 7.84 (t, 2H, J = 7 Hz, H-6, H-6'), 8.07 (d, 2H, J = 8 Hz, H-5, H-5'), 8.50 (s, 2 H, H-2, H-2'); ms: m/z 370 (^{80}Se, $M^{+\cdot}$).

Anal. Calcd. for $C_{18}H_{10}O_4Se$: C, 58.55; H, 2.73. Found: C, 58.70; H, 2.65.

3, 3'-Selenobis-(7-methoxy-4*H*-[1]-benzopyran-4-one) (**5b**).

The yield was 287.5 mg (59%), mp 232°; ir (potassium bromide): 3428, 3061, 1616, 1550, 1437, 1363, 1268, 1198, 1072, 873, 771, 688 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 3.90 (s, 6H, -OCH_3-7, -OCH_3-7'), 7.09 (d, 2H, J = 9 Hz, H-6, H-6'), 7.15 (s, 2H, H-8, H-8'), 7.96 (d, 2H, J = 9 Hz, H-5, H-5'), 8.38 (s, 2H, H-2, H2'); ms: m/z 430 (^{80}Se, $M^{+\cdot}$).

Anal. Calcd. for $C_{20}H_{14}O_6Se$: C, 55.96; H, 3.29. Found: C, 55.87; H, 3.16.

3, 3'-Selenobis-(8-methyl-4*H*-[1]-benzopyran-4-one) (**5c**).

The yield was 312 mg (64%), mp 234.5°; ir (potassium bromide): 3431, 2917, 1655, 1560, 1476, 1459, 1306, 1209, 1107, 1066, 871, 758 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 2.44 (s, 6H, CH_3-8, -CH_3-8'), 7.42 (t, 2H, J = 8 Hz, H-6, H-6'), 7.70 (d, 2H, J = 7 Hz, H-7, H-7'), 7.91 (d, 2H, J = 8 Hz, H-5, H-5'), 8.52 (s, 2H, H-2, H-2'); ms: m/z 398 (^{80}Se, $M^{+\cdot}$).

Anal. Calcd. for $C_{20}H_{14}O_4Se$: C, 60.46; H 3.55. Found: C, 60.53; H, 3.77.

3, 3'-Selenobis-(6-methyl-4*H*-[1]-benzopyran-4-one) (**5d**).

The yield was 331 mg (68%), mp 215°; ir (potassium bromide): 3429, 3060, 1636, 1614, 1479, 1306, 1228, 1112, 1070, 923, 870, 783, 716, 631 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 2.44 (s, 6H, CH_3-6, -CH_3-6'), 7.58 (d, 2H, J = 9 Hz, H-8, H-8'), 7.66 (d, 2H, J = 9 Hz, H-7, H-7'), 7.85 (s, 2H, H-5, H-5'), 8.44 (s, 2H, H-2, H-2'); ms: m/z 398 (^{80}Se, $M^{+\cdot}$).

Anal. Calcd. for $C_{20}H_{14}O_4Se$: C, 60.46: H, 3.55. Found: C, 60.23; H, 3.44.

3,3'-Selenobis-(7-fluoro-4*H*-[1]-benzopyran-4 one) (**5e**).

The yield was 293 mg (60%), mp 250°; ir (potassium bromide): 3427, 3058, 1645, 1615, 1436, 1353, 1293, 1255, 1174, 1070, 953, 875, 850, 770, 684 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 7.43-8.15 (m, 6H, H-5, H-5', H-6, H-6', H-8, H-8'), 8.51 (s, 2H, H-2, H-2'); ms: m/z 406 (^{80}Se, $M^{+\cdot}$).

Anal. Calcd. for $C_{18}H_8F_2O_4Se$: C, 53.35; H, 1.99. Found: C, 53.00; H, 1.84.

3,3'-Di(8-methyl-4-oxo-4*H*-[1]benzopyran)hydroxyselenonium 3-Chlorobenzoate (**6**).

To a stirred solution of *m*-CPBA (230 mg, 1 mmole, 75%) in tetrachloromethane (15 ml) was added **5c** (400 mg, 1 mmole) in chloroform (10 ml). The reaction mixture was cooled and allowed to stand at room temperature for 7 days to give colorless, analytically pure crystals (120 mg, 20%), mp 137°; ir (potassium bromide): 3417, 3058, 1643, 1611, 1570, 1478, 1456, 1422, 1377, 1293, 1257, 1214, 1151, 1119, 1068, 878, 811, 756, 707, 673 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 2.47 (s, 6H, CH_3-8, CH_3-8'), 7.45-7.91 (m, 10H, arom), 8.69 (s, 2H, H-2, H-2'), 13.34 (s, 1H, -OH, exchangeable); ms: FAB^+ m/z 415 (^{80}Se, MH^+-m-CBA).

Anal. Calcd. for $C_{27}H_{19}ClO_7Se$: C, 56.80; H 3.35. Found: C, 55.92; H, 3.09.

3,3'-Bis (8-methyl-4-oxo-4*H*-[1]benzopyran)selenoxide (**7**).

A suspension of **6** (80 mg, 0.19 mmole) in acetone (10 ml) was refluxed for 2 minutes. Upon cooling selenoxide **7** precipitated as colorless crystals (44 mg, 78%) and was recrystallized from acetone, mp 224°; ir (potassium bromide): 3421, 3046, 1644, 1568, 1479, 1457, 1421, 1379, 1295, 1213, 1152, 1118, 1067, 876, 813, 760 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 2.47 (s, 6H, CH_3-8, -CH_3-8'), 7.47 (t, 2H, J = 7 Hz, H-6, H-6'), 7.77 (d, 2H, J = 7 Hz, H-7, H-7'), 7.90 (d, 2H, J = 8 Hz, H-5, H-5'), 8.69 (s, 2H, H-2, H-2'); ms: FAB^+ m/z 415 (^{80}Se, MH^+).

Anal. Calcd. for $C_{20}H_{14}O_5Se$: C, 57.98; H, 3.41. Found: C, 58.14; H, 3.55.

3-(3-Chlorobenzoyl)-2-ethoxy-8-methyl-2,3-dihydro-4-oxo-4*H*-[1]benzopyran-3-ylseleno-3'-(8'-methyl-4'*H*-[1]benzopyran-4'-one) (**8**).

To a solution of **5c** (400 mg, 1 mmole) in chloroform (25 ml) was added *m*-CPBA (75%, 230 mg, 1 mmole). The solution was stirred at room temperature for 72 hours. The solvent was removed by evaporation under reduced pressure and the residue dissolved in ethanol (25 ml). After cooling at 6° for 7 days pale yellow crystals (82 mg, 14%) were collected, dried and recrystallized from acetone-water, mp 161°; ir (potassium bromide): 3428, 3063, 2971, 1733, 1686, 1653, 1596, 1556, 1475, 1305, 1285, 1251, 1183, 1062, 973, 870, 813, 765, 748, 671 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 1.22 (t, 3H, J = 7 Hz, CH_2-CH_3), 2.31 (s, 3H, CH_3-8), 2.42 (s, 3H, CH_3-8'), 3.91-4.12 (m, 2H, -CH_2-CH_3), 6.06 (s, 1H, H-2), 7.13-8.03 (m, 10H, arom), 8.58 (s, 1H, H-2'); ms: FAB^+ m/z 599 (^{35}Cl, ^{80}Se, MH^+).

Anal. Calcd. for $C_{29}H_{23}ClO_7Se$: C, 58.15; H, 3.87. Found C, 58.06; H, 3.89.

2,3-Diethoxy-8-methyl-2,3-dihydro-4-oxo-4*H*-[1]benzopyran-3-ylseleno-3'-(8'-methyl-4'*H*-[1']benzopyran-4'-one) (**9**).

The procedure was the same as described above. Instead of **8**, compound **9** was isolated selectively only once and recrystallized from acetone-water to give **9** (75 mg, 15%) as pale yellow crystals, mp 179°; ir (potassium bromide): 3424, 2969, 2927, 2895, 1680, 1632, 1597, 1564, 1476, 1459, 1378, 1328, 1307, 1288, 1212, 1179, 1151, 1112, 1063, 993, 970, 877, 755, 662 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 1.06 (t, 3H, J = 6 Hz, -CH_2-CH_3), 1.22 (t, 3H, J = 7 Hz, -CH_2-CH_3'), 2.22 (s, 3H, CH_3-8), 2.46 (s, 3H, CH_3-8'), 3.65-4.02 (m, 4H, -CH_2-CH_3), 5.54 (s, 1H, H-2'), 7.01-7.89 (m, 6H, arom), 8.42 (s, 1H, H-2); ms: FAB^+ m/z 489 (^{80}Se, MH^+).

Anal. Calcd. for $C_{24}H_{24}O_6Se$: C, 59.02; H, 4.95. Found: C, 59.04; H, 4.98.

General Procedure for the Preparation of **13a-c**.

To a solution of **5a** (300 mg, 0.81 mmole), **5b** (300 mg, 0.69 mmole) and **5c** (300 mg, 0.75 mmole) in chloroform (25 ml) was added *m*-CPBA (75%, 500 mg, 2.18 mmoles) and the reaction mixtures were stirred at room temperature for 72 hours to give yellow solutions. The solvent was evaporated and the residue was triturated with ethanol (25 ml). The thus obtained solids were filtered off, dried and recrystallized from ethyl acetate to give **13a** (68 mg, 19%), **13b** (80 mg, 22%) and **13c** (73 mg, 20%) as yellow crystals.

3,3'-Diselenobis (4*H*-[1]benzopyran-4-one) (**13a**).

This compound had mp 163.5°; ir (potassium bromide): 3430, 3037, 1644, 1605, 1546, 1459, 1363, 1340, 1309, 1249, 1211, 1161, 1107, 1069, 1019, 887, 875, 759, 689, 614 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 7.56 (t, 2H, J = 7 Hz, H-7, H-7'), 7.71 (d, 2H, J = 8 Hz, H-8, H-8'), 7.87 (t, 2H, J = 8 Hz, H-6, H-6'), 8.08 (d, 2H, J = 8 Hz, H-5, H-5'), 8.81 (s, 2H, H-2, H-2'); ms: m/z 450 (^{80}Se, $M^{+\bullet}$).

Anal. Calcd. for $C_{18}H_{10}O_4Se_2$: C, 48.01; H, 2.24. Found: C, 47.52; H, 1.99.

3,3'-Diselenobis-(7-methoxy-4*H*-[1]benzopyran-4-one) (**13b**).

This compound had mp 213°; ir (potassium bromide): 3422, 3048, 1612, 1550, 1496, 1436, 1357, 1299, 1268, 1233, 1197, 1071, 1018, 936, 873, 837, 770, 687 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 3.91 (s, 6H, OCH_3-7, OCH_3-7'), 7.13 (d, 2H, J = 9 Hz, H-6, H-6'), 7.20 (s, 2H, H-8, H-8'), 8.98 (d, 2H, J = 9 Hz, H-5, H-5'), 8.74 (s, 2H, H-2, H-2'); ms: m/z 510 (^{80}Se, $M^{+\bullet}$).

Anal. Calcd. for $C_{20}H_{14}O_6Se_2$: C, 47.07; H, 2.77. Found: C, 47.4; H, 3.05.

3,3'-Diselenobis-(8-methyl-4*H*-[1]benzopyran-4-one) (**13c**).

This compound had mp 192°; ir (potassium bromide): 3424, 3045, 1735, 1643, 1594, 1555, 1477, 1456, 1423, 1365, 1332, 1307, 1211, 1153, 1111, 1066, 904, 872, 814, 763 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 2.47 (s, 6H, CH_3-8, CH_3-8'), 7.43 (t, 2H, J = 8 Hz, H-6, H-6'), 7.72 (d, 2H, J = 7 Hz, H-7, H-7'), 7.91 (d, 2H, J = 8 Hz, H-5, H-5'), 8.87 (s, 2H, H-2, H-2'); ms: m/z 478 (^{80}Se, $M^{+\bullet}$).

Anal. Calcd. for $C_{20}H_{14}O_4Se_2$: C, 50.22; H, 2.95. Found C, 50.33; H, 2.99.

2-Ethoxy-3-hydroxy-8-methyl-4*H*-[1]benzopyran-4-one (**15**).

This compound was obtained in the same reaction described above for the preparation of **13c**. In this case the ethanolic filtrate (25 ml) was concentrated under reduced pressure to a volume of 5 ml. Preparative thin layer chromatography, performed on Merck Kieselgel 60 F 254 silicagel plates, 2 mm in thickness, using chloroform as development solvent yielded **16** (Rf 0.15, 27 mg, 16%) as a solid after eluation with acetone (3 x 20 ml) and evaporation of the solvent under reduced pressure. Recrystallization from methanol yielded **15** (27 mg, 16%) as colorless crystals, mp 186°; ir (potassium bromide): 3267, 1559, 1390, 1200, 1032, 827, 686 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 1.43 (t, 3H, J = 7 Hz, $-CH_2-CH_3$), 2.51 (s, 3H, CH_3), 4.56 (q, 2H, J = 7 Hz, $-CH_2-CH_3$), 7.34 (t, 1 H, J = 7 Hz, H-6), 757 (d, 1 H, J = 7 Hz, H-7), 7.88 (d 1H, J = 7 Hz, H-5), 8.35 (s, 1H, -OH, exchangeable); ms: m/z 220 ($M^{+\bullet}$).

Anal. Calcd. for $C_{12}H_{12}O_4 \cdot 1/2\ H_2O$: C, 62.87; H, 5.28. Found: C, 62.76, H, 5.46.

3-Ethoxy-2-hydroxy-8-methyl-4*H*-[1]benzopyran-4-one (**21**).

A solution of 2-hydroxy-3-methylbenzoic acid **16** (500 mg, 3.3 mmoles) in thionyl chloride (5 ml) was refluxed for 1 hour. The excess thionyl chloride was evaporated under reduced pressure to give acid chloride **17** (550 mg, 3.23 mmoles) as an oily product. Compound **17** in dry methanol (10 ml) was refluxed for 2 hours. Evaporation of the solvent gave ester **18** as an oily product (530 mg, 3.19 mmoles) that was refluxed with a solution of ethoxy acetic acid chloride (500 mg, 4.1 mmoles) [7] in dry cyclohexane (30 ml) for 2 hours. Evaporation of the solvent under reduced pressure gave an oily product **20**, that was dissolved in chloroform (30 ml). The organic phase was washed with 1*N* sodium hydroxide (2 x 5 ml) and water (3 x 20 ml) and dried with sodium sulfate. The solvent was concentrated *in vacuo* to give **20** as an oil (180 mg, 0.71 mmole). To a suspension of **20** (180 mg) in absolute cyclohexane (30 ml) was added sodium hydride (100 mg, 4.17 mmoles). The mixture was refluxed for 4 hours, after which time the solution was treated with water and acidified (*p*H 1) with dilute hydrochloric acid. The organic and aqueous layers were mixed by stirring whereupon pale yellow crystals precipitated from the aqueous layer. Recrystallization from ethanol afforded **21** (48 mg, 7%) as colorless crystals. The oily intermediate products were monitored by using tlc (chloroform), mp 122°; ir (potassium bromide): 3493, 3405, 2983, 1679, 1626, 1602, 1194, 1098, 764, 744 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 1.28 (t, 3H, J = 7 Hz, CH_2CH_3), 2.36 (s, 3H, $-CH_3$), 4.01 (q, 2H, J = 7 Hz, $-CH_2-CH_3$), 7.25 (t, 1H, J = 7 Hz, H-6), 7.44 (d, 1H, J = 7 Hz, H-7), 7.66 (d, 1H, J = 7 Hz, H-5), 11.68 (s, 1H, -OH, exchangeable); ms: m/z 220 ($M^{+\bullet}$).

Anal. Calcd. for $C_{12}H_{12}O_4 \cdot H_2O$: C, 60.49; H, 5.92. Found: C, 60.77, H, 5.92.

8-Methyl-4-oxo-4*H*-[1]benzopyran-3-seleninic Acid (**22**).

To a suspension of compound **13c** (100 mg, 0.21 mmole) in dioxane (5 ml) was added 35% hydrogenium peroxide (0.5 ml). The resulting mixture was heated for an appropriate time to give a colorless solution. After cooling, water (15 ml) was added and the solution allowed to stand at room temperature for 24 hours. The solid separated was filtered giving pure **22** (95 mg, 94%) as colorless plates, mp 133° dec; ir (potassium bromide): 3425, 3055, 2290, 1631, 1614, 1589, 1562, 1482, 1388, 1309, 1217, 1151, 1128, 1069, 809, 764, 673 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 2.49 (s, 3 H, $-CH_3$), 7.47 (t, 1 H, J = 7 Hz, H-6), 7.77 (d, 1 H, J = 7 Hz, H-7), 7.94 (d, 1 H, J = 7 Hz, H-5), 8.61 (s, 1 H, H-2); rns: m/z 240 (^{80}Se, $M^{+\bullet}$).

Anal. Calcd. for $C_{10}H_8O_4Se$: C, 44.13; H, 2.96. Found: C, 44.13; H, 2.90.

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