Selenium Dioxide Oxidation of Alkylcoumarins and Related Methyl-Substituted Heteroaromatics [1]

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By the use of selenium dioxide as the specific oxidizing agent in the coumarin series, the 4-ethyl, 4-propyl and 4-benzyl substituents of coumarin were converted into α-alcohols **2** and/or ketones **3**, while 3-methyl- and 3-benzylcoumarins were converted into 3-acyl derivatives **7**. The methyl substituent of the analogous thiocoumarin **5**, chromones **10** or thiochromone **11** was also oxidized into the formyl functionality. Facile oxidative desulfurization into the ketone functionality, prior to methyl oxidation, was observed for the thione derivatives of **1a**, **5**, **6** and **10**.

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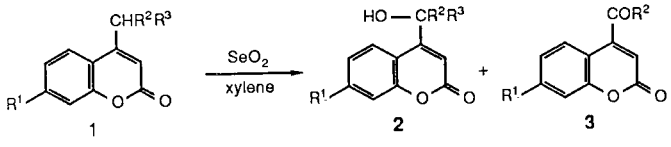
Selenium dioxide has been recognized as an effective reagent for the incorporation of an oxygen functionality at the allylic positions [2], and the reagent has been applied for the preparation of 4-formyl derivatives of coumarins [3-4] and 2(1*H*)-quinolinones [5] from the corresponding 4-methyl derivatives. In order to determine the scope and limitations of this oxidation in the field of coumarin and related chemistry, we attempted an extension of the method to other alkylcoumarins, 2-methylchromones, 1,4-dimethyl-2(1*H*)-quinolinone and their sulfur-containing analogs.



a, $R^1 = R^2 = R^3 = H$
b, $R^1 = CH_3O$, $R^2 = CH_3$, $R^3 = H$
c, $R^1 = CH_3O$, $R^2 = C_2H_5$, $R^3 = H$
d, $R^1 = CH_3O$, $R^2 = C_6H_5$, $R^3 = H$
e, $R^1 = CH_3O$, $R^2 = R^3 = CH_3$

Table 1

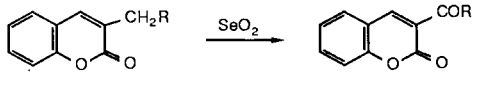
Selenium Dioxide Oxidation of 4-Alkylcoumarins

Substrate	Reaction Time (hour)	Yield [a] (%)	
		2	**3**
1a	8	0	83 [b]
1b	3.5	50	3
1c	8	34	20
1d	3	0	91
1e	6	0	0
2a	6.5	—	89
2b	9	—	16
2c	17	—	90

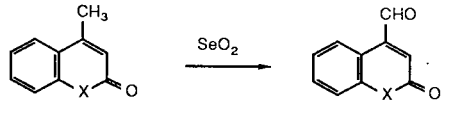
[a] Yield of isolated pure product. [b] Data reported in ref [4].

As shown in Table 1, the 4-alkyl substituents of **1b**, **1c** were oxidized into alcohols **2b** and **2c** accompanied by ketones **3b** and **3c** by the use of 1.5 molar amounts of selenium dioxide in refluxing xylene, while **1d** was smoothly oxidized into **3d** in high yield, similarly to **1a** [4]. The isopropyl substituent of **1e** was totally unaffected under the reaction conditions employed. Oxidation of **1** into **3** appears to involve, at least in part, the intermediate formation of **2**, since conversion of **2** into **3** under the same condition was demonstrated for **2a-c** (Table 1). However, all of the generated **2b** in the reaction of **1b** was not necessarily converted into **3b** or any other products such as coumarin-4-carboxylic acid even after long refluxing with addition of further amounts of the oxidizing agent, and hence the plausible mechanism [6] leading to **2** or **3** directly from **1** cannot be excluded.

Other alkylcoumarins and related methyl-substituted heteroaromatics were subjected to selenium dioxide oxidation under the selected reaction conditions, *i.e.*, at 40-50°



a: R = H; **b** R = C_6H_5



5, **8** : X = S; **6**, **9** : X = NCH_3

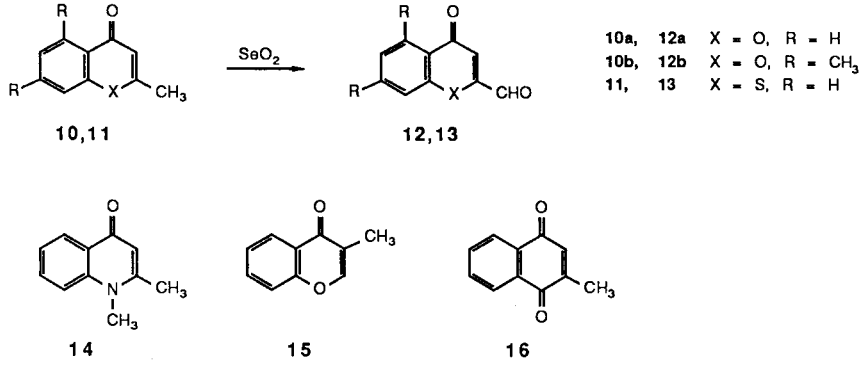
in dioxane (Method A), refluxing in dioxane (Method B), refluxing in benzene (Method C), refluxing in xylene (Method D) or at 170-180° without solvent (Method E). Selection of the method and use of a suitable amount of the reagent were required to attain good yield of the product (see Table 2).

Table 2

Selenium Dioxide Oxidation of Alkylcoumarins and Related Methyl-substituted Heterocycles

Substrate	Molar Ratio SeO_2/Substrate	Method [a]	Reaction Time (hour)	Product	Yield [b] (%)
1a	1.5	B	8	[c]	—
1a	1.5	D	8	**3a**	83 [d]
1a	1.2	E	0.7	**3a**	92
4a	2.0	D	10	[c]	—
4a	2.0	E	3	**7a**	50
4b	2.0	C	10	[c]	—
4b	2.0	D	10	**7b**	15
4b	2.0	E	3	**7b**	94
5	2.0	D	13	**8**	50
6	2.0	D	24	**9**	76
6	1.0	E	0.7	**9**	98
10a	1.5	D	9	**12a**	42
10b	1.5	D	7	**12b**	33
11	2.0	B	5	**13**	40
11	2.0	D	6	**13**	26
17	0.6	A	3	**1a**	61
18	0.6	A	1.5	**5**	23
19	2.0	C	9.5	**6**	49
20	0.6	[e]	0.7	**10a**	71

[a] See the text. [b] Yield of the isolated pure product. [c] No reaction occurred. [d] Data reported in ref [4]. [e] Room temperature in dioxane.



Alkyl substituents of 3-alkylcoumarins **4** and 4-methylcoumarin analogs **1a**, **5**, **6** were oxidized into acyl substituent by Method D or, preferably, by Method E. Similarly to **1a** and **5**, the 2-methyl substituent attached to chromones **10** and thiochromone **11** were also oxidized into the formyl functionality in moderate yields. Contrary to the previous report [7] carried out in dioxane-water solvent, chromone-2-carboxylic acid was not detected in the reaction of **10a**. Analogous **14** was rather sensitive to the selenium dioxide oxidation resulting in degradation into several unidentified products, while the methyl substituent of 3-methylchromone **15** and 2-methyl-1,4-benzoquinone **16** were inert to the reaction.

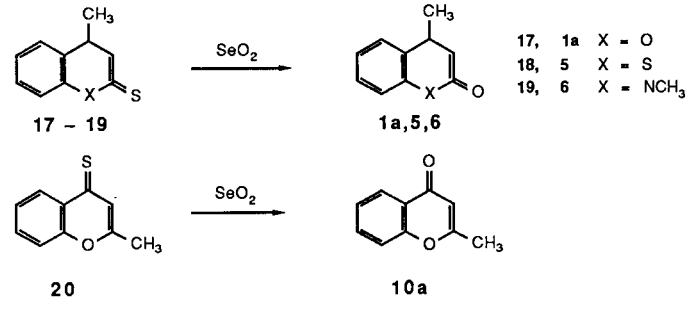


Table 3

Physical and Analytical Data

Compound	MP (°C)	Recrystallization Solvent	Molecular Formula (MW) or Reference MP (°C)	Analysis % Found C	H	S	Calcd. C	H	S
1b	92-93	Methanol	100-101 [19]						
1c	62-65	Methanol	76-78 [20]						
1d	145-147	Methanol	140-141 [21]						
1e	68-70	2-Propanol	$C_{13}H_{14}O_3$ (218.2)	71.55	6.54		71.54	6.47	
2a	139-140	Water	137-138 [22]						
2b	116-118	Benzene	$C_{12}H_{12}O_4$ (220.2)	65.40	5.48		65.44	5.49	
2c	70-71	Petroleum Ether	$C_{13}H_{14}O_4$ (234.2)	66.75	6.11		66.65	6.02	
3b	141	2-Propanol	$C_{12}H_{10}O_4$ (218.2)	65.80	4.38		66.05	4.62	
3c	122-124	Hexane	$C_{13}H_{12}O_4$ (232.2)	67.34	4.96		67.23	5.21	
3d	104-105	2-Propanol	$C_{17}H_{12}O_4$ (280.3)	72.71	4.34		72.85	4.32	
7a	132-133	Benzene	131-132 [26]						
7b	132-135	2-Propanol	135-136 [27]						
8	138-140	2-Propanol	$C_{10}H_6O_2S$ (190.2)	63.23	3.26	16.55	63.14	3.18	16.85
12a	162-164	Ethyl Acetate	162-163 [7]						
12b	145-147	Ethyl Acetate	$C_{12}H_{10}O_3$ (202.2)	71.56	4.99		71.28	4.99	
13	187-188	2-Propanol	$C_{10}H_6O_2S$ (190.2)	63.13	3.25	16.86	63.14	3.18	16.85
17	117-118	2-Propanol	118.5 [23]						
18	112-114	2-Propanol	$C_{10}H_8S_2$ (192.3)	62.42	4.03	33.45	62.46	4.20	33.35
19	159-160	Ethanol	138 [24]						
20	88-90	Ethanol	95 [25]						

Table 4

Spectral Data

Compound	IR (Potassium bromide) cm^{-1}	^{1}H-NMR ppm	MS m/e (%)
1b	1728, 1627, 1293 1153	1.32 (t, 3H, J = 7.6 Hz), 2.78 (q, 2H, J = 7.6 Hz), 3.88 (s, 3H), 6.16 (s, 1H), 6.82-6.92 (m, 2H), 7.54 (d, 1H, J = 9.5 Hz)	204 (M^+, 100), 176 (83), 161 (88), 133 (5), 115 (6)
1c	1715, 1607, 1209 1133	1.04 (t, 3H, J = 7.6 Hz), 1.54-1.84 (m, 2H), 2.70 (t, 2H, J = 7.6 Hz), 3.87 (s, 3H), 6.12 (s, 1H), 6.79-6.91 (m, 2H), 7.52 (d, 1H, J = 9.5 Hz)	218 (M^+, 100), 203 (16), 190 (58), 175 (22), 162 (46), 161 (33)
1d	1717, 1615, 1396 1287, 1144	3.85 (s, 3H), 4.05 (s, 2H), 5.98 (s, 1H), 6.74-6.86 (m, 2H), 7.27-7.30 (m, 5H), 7.52 (d, 1H, J = 9.7 Hz)	250 (M^+, 100), 222 (31), 221 (52), 207 (14), 178 (15), 145 (20), 115 (14)
1e	1727, 1609, 1282 1203, 1133	1.31 (d, 6H, J = 6.8 Hz), 3.18-3.38 (m, 1H), 3.87 (s, 3H), 6.17 (s, 1H), 6.87-6.92 (m, 2H), 7.57 (d, 1H, J = 9.3 Hz)	218 (M^+, 77), 190 (36), 175 (100), 163 (46), 115 (8), 105 (10)
2a	3359, 1671, 1448 1189, 1089	2.84 (br s, 1H), 4.94 (d, 2H, J = 1.3 Hz), 6.66 (t, 1H, J = 1, 4 Hz), 7.25-7.56 (m, 4H)	176 (M^+, 100), 148 (52), 147 (64), 131 (37), 119 (27), 91 (59)
2b	3455, 1689, 1600 1410, 1284, 1202 1118	1.58 (d, 3H, J = 6.6 Hz), 2.47 (br s, 1H), 3.87 (s, 3H), 5.19 (q, 1H, J = 6.4 Hz), 6.48 (s, 1H), 6.76-6.91 (m, 2H), 7.56 (d, 1H, J = 8.9 Hz)	220 (M^+, 100), 192 (19), 177 (29), 175 (23), 121 (19)
2c	3448, 1693, 1610 1284, 1122	1.07 (t, 3H, J = 7.3 Hz), 1.55-1.96 (m, 3H), 2.24 (br s, 1H), 3.87 (s, 3H), 6.44 (s, 1H), 6.79-6.90 (m, 2H), 7.55 (d, 1H, J = 9.5 Hz)	234 (M^+, 100), 206 (47), 178 (47), 177 (84), 121 (58), 77 (26)

Table 4 (continued)

Compound	IR (Potassium bromide) cm^{-1}	^1H-NMR ppm	MS m/e (%)
3b	1730, 1692, 1612 1603, 1358, 1245 1118	2.62 (s, 3H), 3.89 (s, 3H), 6.52 (s, 1H), 6.83-6.93 (m, 2H), 7.88 (d, 1H, J = 9.8 Hz)	218 (M^+, 100), 204 (22), 190 (34), 176 (20), 175 (67)
3c	1724, 1694, 1614 1295	1.25 (t, 3H, J = 7.3 Hz), 2.91 (q, 2H, J = 7.3 Hz), 3.89 (s, 3H), 6.43 (s, 1H), 6.82-6.92 (m, 2H), 7.71 (d, 1H, J = 9.8 Hz)	232 (M^+, 100), 218 (12), 203 (33), 176 (20), 175 (67), 131 (25), 119 (16)
3d	1740, 1660, 1619 1292, 1145	3.89 (s, 3H), 6.26 (s, 1H), 6.74-8.00 (m, 8H)	280 (M^+, 100), 252 (35), 224 (10), 209 (10), 175 (24), 105 (39), 77 (31)
7a	1729, 1695, 1601 1177	7.36-7.78 (m, 4H), 8.44 (s, 1H), 10.27 (s, 1H)	174 (M^+, 100), 147 (49), 145 (49), 119 (22), 101 (21), 90 (93), 89 (84)
7b	1727, 1663, 1612 1567, 1445, 1270 1243, 1162	7.28-7.94 (m, 9H), 8.08 (s, 1H)	250 (M^+, 100), 221 (64), 194 (11), 173 (26), 145 (9), 105 (92), 77 (87)
8	1705, 1633, 1582 1428, 1232, 1120	6.95 (s, 1H), 7.45-7.58 (m, 3H), 8.80-8.90 (m, 1H), 10.16 (s, 1H)	190 (M^+, 91), 176 (33), 162 (91), 161 (91), 147 (54), 134 (100), 133 (61)
12a	1705, 1658, 1607 1470, 1408, 1118	6.91 (s, 1H), 7.39-7.81 (m, 3H), 8.16-8.26 (m, 1H), 9.80 (s, 1H)	174 (M^+, 100), 146 (28), 145 (25), 120 (20), 92 (24), 89 (20)
12b	1711, 1658, 1616 1482, 1400	2.41 (s, 3H), 2.76 (s, 3H), 6.74 (s, 1H), 6.96 (s, 1H), 7.16 (s, 1H), 9.70 (s, 1H)	202 (M^+, 41), 173 (8), 150 (10), 149 (100), 111 (11), 105 (12)
13	1692, 1615, 1590 1437, 1083	7.52 (s, 1H), 7.66-7.73 (m, 3H), 8.46-8.53 (m, 1H), 9.89 (s, 1H)	190 (M^+, 100), 162 (22), 161 (36), 136 (43), 134 (11), 108 (21), 89 (25)
17	1599, 1549, 1389 1290, 1270, 1158 1139, 1105, 1069	2.38 (d, 3H, J = 1.2 Hz), 7.18 (d, 1H, J = 1.2 Hz), 7.40-7.72 (m, 4H)	176 (M^+, 100), 160 (9), 132 (96), 131 (46), 115 (11)
18	1579, 1528, 1240 1220, 1159, 1060 1009	2.48 (d, 3H, J = 1.2 Hz), 7.44-7.53 (m, 4H), 7.85-7.95 (m, 1H)	192 (M^+, 100), 177 (15), 148 (93), 147 (63), 115 (13)
19	1615, 1559, 1445 1343, 1154, 1059	2.44 (s, 3H), 4.33 (s, 3H), 7.60 (s, 1H), 7.32-7.74 (m, 4H)	189 (M^+, 100), 173 (7), 144 (31), 143 (38), 121 (9), 115 (13)
20	1612, 1558, 1391 1280, 1158	2.34 (s, 3H), 7.15 (s, 1H), 7.30-7.80 (m, 3H), 8.51-8.60 (m, 1H)	176 (M^+, 100), 161 (5), 147 (12), 132 (20), 131 (30), 121 (6), 115 (12), 108 (10)

A variety of reagents have been reported so far [8] for the transformation of thioketones into ketones. We found that selenium dioxide was effective for the oxidative desulfurization of the thione functionality of 4-methylcoumarin-2-thione analogs **17-19** and also 2-methylchromone-4-thione **20**, which were readily carried out in dioxane at lower temperature (except for **19**) by the use of a 0.6 molar amount of selenium dioxide. Reaction of **18** with an excess amount of the reagent in refluxing xylene (Method D) afforded a mixture of **5** and **8**, suggesting facile desulfurization prior to oxidation of the 4-methyl functionality.

EXPERIMENTAL

All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Infrared spectra were determined using a Hitachi 215 grating spectrophotometer. Mass spectra were taken on a Shimadzu LKB-900B spectrometer (direct inlet, at 70 eV). The ^1H-nmr spectra were recorded at 100 MHz with a JEOL JNM-FX 100 spectrometer or at 270 MHz with a JEOL JNM-GX 270 spectrometer, using tetramethylsilane as an internal standard and deuteriochloroform as a solvent.

The following substrates were prepared by the literature methods quoted: 4-methylcoumarin [9] **1a**, 4-methyl-1-thiocoumarin [10] **5**, 1,4-dimethyl-2(1*H*)-quinolinone [11], **6**, 2-methylchromone [12] **10a**, 2-methyl-1-thiochromone [12] **11**, 1,2-dimethyl-4(1*H*)-quinolinone [13] **14**, and 3-methylchromone [14] **15**. 3-Benzylcoumarin [15] **4b** (mp 103-105°) was prepared by the method of Grimshaw and Haworth [16]. 2,5,7-Trimethylchromone **10b** (mp 55-56° [17]) was donated by Dr. K. Nagasawa of this laboratory. Commercially available 3-methylcoumarin **4a** and 2-methyl-1,4-benzoquinone **16** were used.

4-Alkyl-7-methoxycoumarins **1b-e**. Typical Procedure.

Ethyl 4-methyl-3-oxopentanoate (10.7 g, 68 mmoles), prepared from Meldrum's acid and isobutyryl chloride by the reported procedure [18], resorcinol (5.7 g, 52 mmoles) and concentrated sulfuric acid (25 ml) were combined with stirring, and the mixture was allowed to stand for two days at room temperature. The mixture was poured into ice-water (200 ml), and the resulting precipitate was collected, washed with water and dried. Recrystallization from benzene gave orange plates of 7-hydroxy-4-isopropylcoumarin, mp 62-64°, yield 5.3 g (49%); ir (potassium bromide):

3095, 1680, 1608, 1563, 1313 cm^{-1}; ^{1}H-nmr (deuteriochloroform): δ 1.32 (6H, d, J = 6.3 Hz), 3.15-3.35 (1H, m), 6.20 (1H, s), 6.86-7.63 (3H, m).

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.67; H, 5.99.

To a solution of 7-hydroxy-4-isopropylcoumarin (6.0 g, 29 mmoles) and methyl iodide (23 g, 160 mmoles) in dry acetone (150 ml), anhydrous potassium carbonate (22 g, 160 mmoles) was added and the mixture was refluxed for 2 hours with vigorous stirring. After cooling, the reaction mixture was filtered and the filtrate was concentrated to leave crystals, which were recrystallized from 2-propanol to give prisms of 4-isopropyl-7-methoxycoumarin **1e**, yield 5.3 g (83%).

A similar procedure was followed for 4-ethyl-7-methoxycoumarin [19] **1b** (yield from resorcinol, 64%), 7-methoxy-4-propylcoumarin [20] **1c** (yield from resorcinol, 71%) and 4-benzyl-7-methoxycoumarin [21] **1d** (yield from resorcinol, 78%).

Coumarin-4-methanol (**2a**).

Sodium borohydride (382 mg, 10 mmoles) was added in small portion to a solution of coumarin-4-carboxaldehyde **3a** (3.5 g, 20 mmoles) dissolved in ethanol (100 ml) at 35°, and the mixture was stirred for 2 hours at room temperature. The reaction mixture was concentrated under reduced pressure and the residue was extracted with hot chloroform (3 × 10 ml). The combined extracts were dried over anhydrous magnesium sulfate and filtered. Evaporation of the solvent from the filtrate gave **2a** [22], yield 1.8 g (50%).

4-Methylcoumarin-2-thione Analogs **17-20**. Typical Procedure.

To a solution of 4-methyl-1-thiocoumarin **5** (2.8 g, 16 mmoles) in benzene (50 ml) phosphorus pentasulfide (4.2 g, 19 mmoles) was added and the mixture was vigorously stirred at reflux for 2 hours. The reaction solution was decanted, and the residue was extracted with hot benzene (3 × 30 ml). The hot solution and the extracts were combined and cooled to room temperature. Removal of some precipitates in the resulting mixture by filtration and concentration of the filtrate under reduced pressure, followed by recrystallization of the residue from 2-propanol, gave brown needles of 4-methyl-1-thiocoumarin-2-thione **18**, yield 1.6 g (53%).

A similar procedure was followed for 4-methylcoumarin-2-thione [23] **17** (yield 79%), 1,4-dimethyl-2(1*H*)-quinolinethione [24] **19** (yield 40%) and 2-methylchromone-4-thione [25] **20** (yield 68%).

Selenium Dioxide Oxidation. Typical Procedure.

Powdered selenium dioxide (1.5 g, 13.5 mmoles) was added to a solution of 4-ethyl-7-methoxycoumarin **1b** (1.8 g, 9 mmoles) dissolved in hot xylene (15 ml), and the whole was refluxed for 3.5 hours with vigorous stirring. The process of the reaction was monitored by tlc analysis of the solution. The mixture was filtered hot to remove black selenium, and the filtrate was concentrated under reduced pressure. The residue was subjected to chromatography over silica gel (Wakogel C-200). From the fraction eluted with chloroform—carbon tetrachloride (1:1, v/v) **3b** was obtained, yield 60 mg (3%). Further elution with chloroform—methanol (20:1, v/v) gave **2b**, yield 960 mg (50%).

A similar procedure was followed for the oxidation of the other substrates **1a-d**, **2**, **4-6**, **10-11**, **17-20**. As for the reaction solvent and temperature in Table 2, the following combinations were applied instead of xylene at reflux (Method D); dioxane at 40-50° (Method A), dioxane at reflux (Method B), benzene at reflux (Method C), without solvent at 170-180° (Method E).

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REFERENCES AND NOTES

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