Modification of Hydroxybenzopyranoids: Facile Deoxygenation of 2,2-Dimethyl-7-hydroxy-4-chromanones and a New Approach to Their Novel Mercapto Analogs

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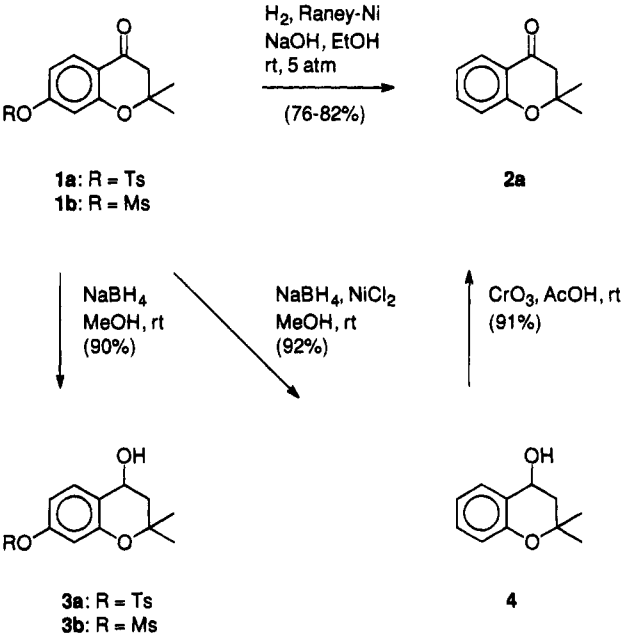
A facile deoxygenation of a systematic series of substituted 2,2-dimethyl-7-hydroxy-4-chromanones *via* their sulfonate, isourea, and thiocarbamate derivatives is reported. The synthesis of novel 2,2-dimethyl-7-mercapto-4-chromanones has been accomplished by the hydrolysis of the corresponding thiocarbamates. The scope and limitations of different deoxygenation procedures in the case of these hydroxybenzopyranoids are also presented.

Introduction

Substituted 2,2-dimethyl-1-benzopyrans of various levels of saturation and oxidation are common natural products which are widely distributed among many plants.[1] Furthermore, they have considerable biological importance, especially as potentially useful modern pesticides[2] and drug candidates in the field of potassium channel openers.[3] Because of their ease of preparation and relative stability, 2,2-dimethyl-4-chromanones have a central role and are valuable intermediates for synthetic purposes in 2,2-dimethyl-1-benzopyran chemistry.[4]

Indeed, there are numerous independent methods available for the preparation of 2,2-dimethyl-4-chromanones, and those procedures of synthetic importance have been reviewed extensively.[5,6] Recently, we have reported on the first systematic study including some mechanistic investigations of the reaction of a series of monosubstituted phenols with 3-methylbut-2-enoic acid in $POCl_3/ZnCl_2$ and $POCl_3/AlCl_3$ (one of the most frequently and successfully applied methods of direct preparation of 2,2-dimethyl-4-chromanones).[7] Our findings indicate that despite successful applications in the case of 3-hydroxy- and 3-alkoxyphenols and further substituted derivatives,[8] these conditions are unsuitable for a similar transformations of cresols or chlorophenols, *i.e.*,

Scheme 1



for direct synthesis of 2,2-dimethyl-*des*-7-hydroxy-4-chromanones.

It can be easily recognized that a facile deoxygenation of 2,2-dimethyl-7-hydroxy-4-chromanones would lead to the formation of such 4-chromanone derivatives which could not be directly prepared, and their synthesis often requires a complicated multistep reaction sequence.[9]

There are several methods available for reductive removal of phenolic hydroxy groups.[10] Among them, reductive transformation of *O*-aryl *p*-toluenesulfonates by $NaBH_4–NiCl_2$[11] or Raney nickel,[12] catalytic hydrogenation of *O*-aryl-*N*,*N*-dialkylisoureas by Pd/C,[13] and desulfurization of *S*-aryl *N*,*N*-dialkylthiocarbamates (readily available by Newman–Kwart rearrangement of

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O-aryl *N,N*-dialkylthiocarbamates) by Raney nickel[14] proved to be the most efficient and widely used procedures of synthetic importance. In addition, since *S*-aryl thiocarbamates are readily hydrolyzed to the corresponding arylmercaptans,[15] we conceived that novel 2,2-dimethyl-7-mercapto-4-chromanones could also be prepared.

Indeed, we report here[16] that a systematic series of substituted 2,2-dimethyl-7-hydroxy-4-chromanones **5a–j** were transformed into their corresponding deoxygenated derivatives **2a–j** and 7-mercapto analogs **10a–j**, respectively. In addition, the scope and limitations of the application of these deoxygenation procedures[10–15] in the case of these hydroxybenzopyranoids are also presented.

Results and Discussion

The starting substituted 2,2-dimethyl-7-hydroxy-4-chromanones **5a–j** were prepared in good overall yields according to the reported procedures.[17]

Sulfonates (Scheme 1). The sulfonates **1a,b** were treated with Raney-nickel in ethanol (containing sodium hydroxide) at room temperature under hydrogen atmosphere (5 atm) for 1 h to furnish the deoxygenated product **2a** in 76–82% yield, but up to 20% 7-hydroxy-chromanone **5a** is also formed. The reduction of sulfonates **1a,b** with $NaBH_4$–$NiCl_2$ in methanol gave 2,2-dimethyl-4-hydroxychroman **4** in practically useful yield (94%). Reduction with only $NaBH_4$ in methanol gave the corresponding 4-hydroxysulfonates **3a,b** in 93% yield. The 4-hydroxychroman **4** can be oxidized back[18] to the 4-chromanone **2a** using CrO_3 in AcOH in good yield (91%). On the basis of these findings we concluded that methods for the reductive transformation of sulfonates **1a,b** had not been proven as the method of choice for our purposes.

Isoureas (Scheme 2). The reaction of 7-hydroxy-4-chromanone **5a** with cyanogen bromide in the presence of triethylamine in dry ether at −5 °C for 0.5 h furnished the corresponding cyanate **6a** in excellent yield (98%). The latter compound was then treated with diethylamine in ether at −5 °C for 0.5 h, and the *O*-aryl *N,N*-diethylisourea **7a** was formed in an almost quantitative yield. Catalytic hydrogenation of this derivative over palladium on activated carbon under hydrogen atmosphere (5 atm) at room temperature gave 2,2-dimethyl-4-chromanone **2a** in good yield. This sequence seemed to be applicable for similar transformation of various 4-chromanones **5b–i** (Table 1). An attempted preparation of 2,2-dimethyl-5-hydroxy-4-chromanone 7-cyanate was unsuccessful, and the corresponding 5,7-dicyanate was obtained. The reason for this observation is the high reactivity of cyanogen bromide even at low temperature. Data show in Table 1 that our approach proved to be superior in most instances (except entry 8; dechlorination took also place) in comparison with those of reported

Scheme 2

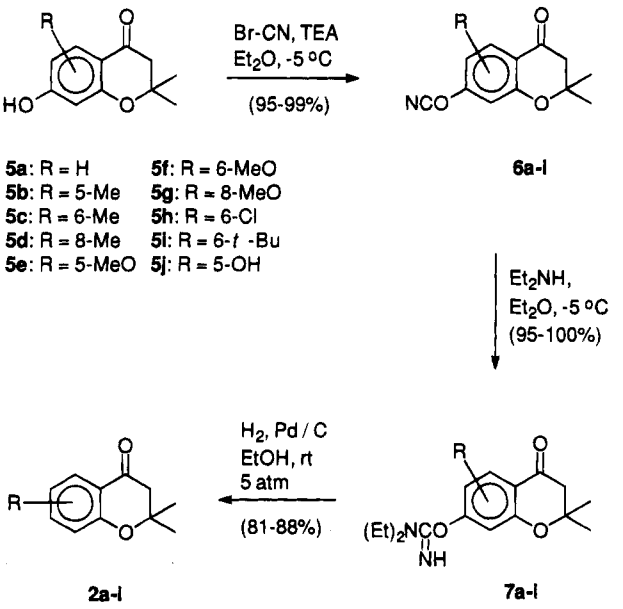

Table 1. Transformation and Deoxygenation of 7-Hydroxy-4-chromanones *via* Their Isourea Derivatives

entry	substrate	yields[a] (%) 6	7	2	overall yield[b] (%)	reported yield[c] (%)
1	**5a**	98	100	87	85	65[27]
2	**5b**	99	95	86	80	–[20]
3	**5c**	99	98	85	82	–[21]
4	**5d**	100	98	82	80	8[20]
5	**5e**	97	98	86	81	15[9b]
6	**5f**	100	95	82	78	82[19]
7	**5g**	100	97	81	78	36[22]
8	**5h**	98	97	86[d]	81	79[27]
9	**5i**	97	99	88	84	–

[a] Yields of individual steps. [b] Yield of **2** based on **5**. [c] Best literature yields. [d] Yield of **2a**.

procedures[9,19–22] for the preparation of the corresponding 5-, 6-, or 8-substituted 2,2-dimethyl-4-chromanones.

In the case of 5-, 6-, and 8-methyl derivatives **2b,c,d** no yields were reported[20,21] (except for 2,2,8-trimethyl-4-chromanone **2d**); in addition, these compound were characterized only by melting points and elemental analyses, which are definitely not enough for these close regioisomers. According to the reported procedure the 2,2-dimethyl-5-methoxy-4-chromanone **2e** can be prepared in 15% yield *via* a complicated multistep sequence,[9b] and the corresponding 8-methoxy derivative **2g** is available from 8-methoxycoumarin by the five-step synthesis in 36% yield.[22] The 2,2-dimethyl-6-methoxy-4-chromanone **2f** can be prepared *via* photo-Fries rearrangement of the corresponding 4-(methoxyphenyl)-3-methylbut-2-enoate in 82% yield.[19] It is worth noting, that this above method is restricted to this particular substitution pattern; *i.e.*, there is no possibility for *p*-Fries rearrangement.

Dimethylthiocarbamates (Scheme 3). 2,2-Dimethyl-7-hydroxy-4-chromanones **5a–j** were allowed to react with dimethylthiocarbamoyl chloride in the presence of DABCO in DMF at room temperature to yield 2,2-dimethyl-7-((*N,N*-dimethylthiocarbamoyl)oxy)-4-chro-

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Scheme 3

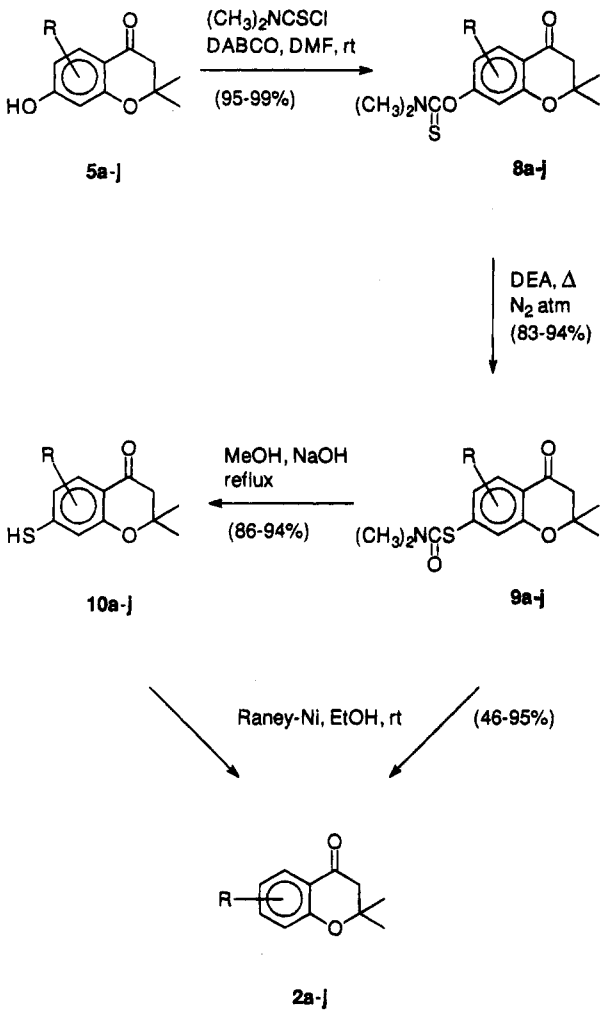

Table 2. Preparation of 2,2-Dimethyl-4-chromanones and Their Mercapto Derivatives *via* Newman–Kwart Rearrangement

		yields[a] (%)				overall yields[b] (%)	
entry	substrate	8	9	10	2	10	2
1	**5a**	98	94	94	87	86	80
2	**5b**	98	92	89	91	80	82
3	**5c**	96	83	92	89	73	71
4	**5d**	95	92	92	91	80	80
5	**5e**	94	93	91	95	79	83
6	**5f**	91	96	86	92	75	80
7	**5g**	92	91	92	93	77	78
8	**5h**	98	91	92	46[c]	82	41
9	**5i**	95	94	90	93	80	83
10	**5j**	90	92	90	85	74	70[d]

[a] Yields of individual steps. [b] Yields based on **5**. [c] 48% **2a** is also formed. [d] Best literature yield 10%.[9a]

manones **8a–j** which were then thermally rearranged into 2,2-dimethyl-7-((*N*,*N*-dimethylcarbamoyl)thio)-4-chromanones **9a–j** in *N*,*N*-diethylaniline. Alkaline hydrolysis of these compounds in methanol resulted in the formation of the novel 2,2-dimethyl-7-mercapto-4-chromanones **10a–j**. Both compounds **9** and **10** were readily desulfurized by Raney-nickel in ethanol at room temperature to furnish the corresponding deoxygenated 4-chromanones **2a–j** in good overall yield (Table 2). In the course of desulfurization of 2,2-dimethyl-6-chloro-7-((*N*,*N*-dimethylcarbamoyl)thio)-4-chromanone (**9h**) partial dechlorination took also place (Table 2, entry 8).

In the case of 5,7-dihydroxy-2,2-dimethyl-4-chromanone (**5j**) the regioselectivity of the acylation made possible the preparation of 2,2-dimethyl-5-hydroxy-4-chromanone (**2j**).

Conclusions

In summary, by the well-known[10–15] deoxygenation procedures a facile deoxygenation of a systematic series of substituted 2,2-dimethyl-7-hydroxy-4-chromanones **5** *via* their sulfonate **1**, isourea **7**, and thiocarbamate **9** derivatives has been achieved in high overall yields. The synthesis of novel 2,2-dimethyl-7-mercapto-4-chromanones **10** has also been accomplished by the hydrolysis of the corresponding thiocarbamates **9**. Deoxygenation of the different sulfonates **1** has a limited value because of the hydrolytic side reactions. Due to the high reactivity of cyanogen bromide, an attempted preparation of 2,2-dimethyl-5-hydroxy-4-chromanone (**2j**) was not possible *via* the corresponding isourea derivative **7j**; on the other hand, **2j** has been successfully obtained *via* the corresponding thiocarbamate derivative **9j**. In the course of the reduction and desulfurization of 2,2-dimethyl-6-chloro-4-chromanone derivatives **7h** and **9h**, respectively, dechlorination took also place. We have demonstrated the convenient preparation of these known and new deoxygenated 2,2-dimethyl-4-chromanone derivatives **2** (which are frequently used intermediates in the syntheses of important biologically active compounds) as a powerful alternative in benzopyran chemistry.

Experimental Section

General. Melting points are uncorrected. ^{1}H-NMR (200 MHz) spectra were recorded in $CDCl_3$ solution, using TMS as internal reference. Mass spectra were obtained in the EI mode (70 eV, direct inlet). Elemental analyses were performed by the Microanalysis Laboratory, L. Kossuth University. Thin layer chromatography was carried out on silica gel plates (E. M. Science 5554, Kieselgel 60F_{254}). Solvents were used either as purchased or dried and purified by standard methodology. Organic solutions were dried over anhydrous Na_2SO_4 and concentrated.

Preparation of the Starting Substrates. The preparation of the following 2,2-dimethyl-4-chromanones was described earlier: **1a**,[23] **1b**,[24] **5a**,[17a] **5b**,[17b] **5c**,[17c] **5d**,[17d] **5f**,[16b] **5h**,[17e] **5i**.[17e] Compounds **5e** and **5g** were prepared in 70% and 65% yields, respectively, from the corresponding 5,7- and 7,8-dihydroxy-2,2-dimethyl-4-chromanones[8b] as described previously.[16b] **2,2-Dimethyl-7-hydroxy-5-methoxy-4-chromanone (5e)**: mp 212–213 °C (from MeOH) (lit.[25] mp 208–209 °C (from EtOH)); ^{1}H NMR δ 1.43 (s, 6H), 2.65 (s, 2H), 3.78 (s, 3H), 6.05 (m, 2H), 8.10 (s, 1H); MS *m*/*z* (relative intensity) 222 (M^+, 33), 208 (48), 207 (38), 193 (100), 166 (47), 153 (58), 138 (30), 137 (50), 124 (32), 96 (18), 69 (64). Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.79 H, 6.39. **2,2-Dimethyl-7-hydroxy-8-methoxy-4-chromanone (5g)**: mp 113–114 °C (from CCl_4); ^{1}H NMR δ 1.50 (s, 6H), 2.68 (s, 2H), 3.93 (s, 3H), 6.26 (s, 1H), 6.60 (d, J = 9 Hz, 1H), 7.58 (d, J = 9 Hz, 1H); MS *m*/*z* (relative intensity) 222 (M^+, 62), 207 (82), 167 (88), 166 (29), 152 (28), 138 (100), 137 (50), 123 (32), 95 (32), 79 (12). Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.90; H, 6.41.

Preparation of Cyanates 6a–i. General Procedure. To a stirred mixture of starting 4-chromanones **5a–i** (10 mmol) and triethylamine (1.5 mL, 10 mmol) in absolute ether (25 mL) was added BrCN (1.16g, 10 mmol) in absolute ether (25 mL) within 15 min at −5 °C. The reaction mixture was stirred for

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a further 15 min, and then the solid was filtered off and washed with ether (10 mL) and the combined washing and the filtrate was evaporated. The residual cyanates **6a–i** were pure enough for further runs. Yields are summarized in Table 1.

7-Hydroxy-2,2-dimethyl-4-chromanone-7-cyanate (6a): mp 51–52 °C; ^{1}H NMR δ 1.48 (s, 6H), 2.74 (s, 2H), 6.92 (m, 2H), 7.96 (d, J = 9 Hz, 1H); MS m/z (relative intensity) 217 (M^+, 26), 202 (100), 177 (11), 162 (58), 133 (10), 119 (11), 107 (8), 91 (13), 77 (15), 63 (20), 55 (26). Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.43; H, 5.22; N, 6.31.

Preparation of Isoureas 7a–i. General Procedure. Cyanates **6a–i** (10 mmol) were dissolved in absolute ether (10 mL), and absolute diethylamine (1.04 mL, 10 mmol) was added at −5 °C with stirring within 15 min. The reaction mixtures were stirred for a further 15 min, and the solvent was evaporated. The residual isoureas **7a–i** were suitably pure for the next step. Yields are summarized in Table 1.

7-Hydroxy-2,2-dimethyl-4-chromanone 7-(*N,N*-diethylisourea) (7a): mp oil; ^{1}H NMR δ 1.21 (t, J = 7 Hz, 6H), 1.47 (s, 6H), 2.71 (s, 2H), 3.30–3.54 (m, 4H), 4.77 (br s, 1H), 6.66 (d, J_2 = 2 Hz, 1H), 6.72 (dd, J_1 = 9 Hz, J_2 = 2 Hz, 1H), 7.88 (d, J_1 = 9 Hz, 1H); MS m/z (relative intensity) 290 (M^+, 1), 192 (2), 177 (3), 98 (24), 83 (25), 69 (12), 55 (100). Anal. Calcd for $C_{16}H_{22}N_2O_3$: C, 66.18; H, 7.64; N, 9.65. Found: C, 66.34; H, 7.43; N, 9.86.

Deoxygenation of Isoureas 7a–i. General Procedure. Isoureas **7a–i** (10 mmol) were dissolved in absolute EtOH (50 mL), treated with 10% Pd/C (0.3 g), and vigorously stirred under hydrogen atmosphere (5 atm) at room temperature. After the starting material was consumed (1–8 h, checked by TLC), the catalyst was filtered off and the solvent was removed. The residues were dissolved in ether (100 mL), and the organic layers were washed with 5% aqueous NaOH (50 mL), 5% aqueous HCl (50 mL), and water (2 × 50 mL) and dried. The residues were crystallized from MeOH affording the corresponding deoxygenated 4-chromanones **2a–i**. Overall yields are summarized in Table 1.

2,2-Dimethyl-4-chromanone (2a): mp 89–90 °C (from EtOH) (lit.[26] mp 87–88 °C (from petroleum ether)); ^{1}H NMR δ 1.48 (s, 6H), 2.64 (s, 2H), 6.96 (m, 2H), 7.47 (m, 1H), 7.86 (dd, J_1 = 2 Hz, J_2 = 10 Hz, 1H); MS m/z (relative intensity) 176 (M^+, 40), 161 (100), 121 (72), 120 (69), 92 (82), 63 (36).

Preparation of 2,2-Dimethyl-7-((*N,N*-dimethylthiocarbamoyl)oxy)-4-chromanones 8a–j. General Procedure. A mixture of 2,2-dimethyl-7-hydroxy-4-chromanones **5a–j** (10 mmol), dimethylthiocarbamoyl chloride (2.48 g, 20 mmol), 1,4-diazabicyclo[2.2.2]octane (2,24 g, 20 mmol), and absolute DMF (30 mL) was stirred at room temperature for 2 h, and then it was poured onto crushed ice (200 g). The separated solid was filtered, washed with 10% aqueous HCl (50 mL) and water, and treated with cold MeOH to afford compounds **8a–j**. Analytical samples were crystallized from MeOH (Table 2).

2,2-Dimethyl-7-((*N,N*-dimethylthiocarbamoyl)oxy)-4-chromanone (8a): mp 157–159 °C (from MeOH); ^{1}H NMR δ 1.47 (s, 6H), 2.73 (s, 2H), 3.33 (s, 3H), 3.46 (s, 3H), 6.66 (d, J_2 = 2 Hz, 1H), 6.72 (dd, J_1 = 8.5 Hz, J_2 = 2 Hz, 1H), 7.89 (d, J_1 = 8.5 Hz, 1H); MS m/z (relative intensity) 279 (M^+, 30), 177 (7), 149 (10), 107 (15), 88 (88), 72 (100). Anal. Calcd for $C_{14}H_{17}NO_3S$: C, 60.19; H, 6.13; N, 5.01; S, 11.48. Found: C, 60.23; H, 6.07; N, 5.31; S, 11.70.

Preparation of 2,2-Dimethyl-7-((*N,N*-dimethylcarbamoyl)thio)-4-chromanones 9a–j. General Procedure. Compounds **8a–j** (10 mmol) were dissolved in *N,N*-dimethylaniline (30 mL), and the reaction mixtures were heated at 200 °C under N_2 atmosphere for 1 h and then poured into 10% aqueous HCl (300 mL). The precipitate was filtered off, washed free of acid, and treated with cold MeOH to obtain substances **9a–j**. Analytical samples were crystallized from MeOH (Table 2).

2,2-Dimethyl-7-((*N,N*-dimethylcarbamoyl)thio)-4-chromanone (9a): mp 123–124 °C (from MeOH); ^{1}H NMR δ 1.46 (s, 6H), 2.72 (s, 2H), 3.07 (br s, 6H), 7.10 (m, 2H), 7.85 (d, J = 8.5 Hz, 1H); MS m/z (relative intensity) 279 (M^+, 5), 95 (8), 72 (100). Anal. Calcd for $C_{14}H_{17}NO_3S$: C, 60.19; H, 6.13; N, 5.01; S, 11.48. Found: C, 60.31; H, 6.24; N, 4.79; S, 11.30.

Desulfurization of 2,2-Dimethyl-7-((*N,N*-dimethylcarbamoyl)thio)-4-chromanones 9a–j by Raney Nickel. A mixture of substances **9a–j** (5 mmol) and Raney nickel (10 g) in EtOH (30 mL) was vigorously stirred at room temperature for 1 h. The solid material was filtered off, the solvent evaporated, the residues were dissolved in ether (100 mL). The organic layers were washed with 10% aqueous HCl (3 × 50 mL) and water (100 mL) and dried. Crystallization from MeOH afforded the corresponding 4-chromanones **2a–j**. Overall yields are summarized in Table 2.

Preparation of 2,2-Dimethyl-7-mercapto-4-chromanones 10a–j. A mixture of 2,2-dimethyl-7-((*N,N*-dimethylcarbamoyl)thio)-4-chromanones **9a–j** (10 mmol), KOH (5.0 g, 75 mmol), and MeOH (50 mL) was stirred at reflux under N_2 atmosphere for 1 h. The solvent was removed in vacuum, and water (50 mL) was added to the residue. This mixture was extracted with Et_2O (3 × 50 mL). The aqueous solution was acidified with concd HCl to pH 1, and the precipitate formed was filtered, washed with water, and dried. Crystallization from MeOH afforded compounds **10a–j** (Table 2).

2,2-Dimethyl-7-mercapto-4-chromanone (10a): mp 87–88 °C (from MeOH); ^{1}H NMR δ 1.46 (s, 6H), 2.70 (s, 2H), 3.62 (s, 1H), 6.80 (m, 2H), 7.71 (d, J = 9 Hz, 1H); MS m/z (relative intensity) 208 (M^+, 72), 192 (100), 153 (97), 152 (68), 124 (18), 96 (30). Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.44; H, 5.81; S, 15.39. Found: C, 63.57; H, 5.97; S, 15.47.

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Supplementary Material Available: ^{1}H NMR, MS, and microanalysis data of **2b–j**, **6b–i**, **7b–i**, **8b–j**, **9b–j**, and **10b–j** (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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