# Selective *ortho*-Alkylation of Phenols with Sulphoxides *via* [2,3]Sigmatropic Rearrangement: Synthesis of Coumarins

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*ortho*-Alkylphenols have been prepared from phenol and dialkyl sulphoxides *via* [2,3]sigmatropic rearrangement, using thionyl chloride or phenyl chlorosulphinate as an activator of sulphoxides. In the same manner, *ortho*-phenylthiomethylphenol has been prepared in good yield. When ethyl phenyl sulphoxide, diallyl sulphoxide, and methyl methylsulphinylacetate were used as sulphoxides, none of the expected products were obtained. Salicylaldehyde has been prepared in moderate yield, when methyl methylthiomethyl sulphoxide was used as a sulphoxide. 3-(2-Hydroxyphenyl)propionic acid derivatives, which were obtained from substituted phenols and dimethyl 3,3'-sulphinyldipropionate, have been cyclized to give the corresponding coumarins in good yields.

Although *ortho*-alkylphenols are useful intermediates in organic synthesis, it is difficult to obtain them selectively by the direct alkylation of phenols. We reported previously that thionyl chloride and phenyl chlorosulphinate were useful activators for dimethyl sulphoxide (DMSO) in the selective preparation of *ortho*-methylthiomethylphenol *via* a [2,3]sigmatropic rearrangement. We also investigated the methylthiomethylation of various substituted phenols.[1]

In this paper, we investigate the selective *ortho*-alkylation of phenols with various sulphoxides activated by thionyl chloride or phenyl chlorosulphinate. Moreover, we report the preparation of salicylaldehyde and substituted coumarins using a [2,3]sigmatropic rearrangement as a key step.

The mechanism of the reaction of phenol and sulphoxides is illustrated in Scheme 1. The reaction of phenol with DMSO (**1a**) afforded *o*-methylthiomethylphenol in good yields, when either thionyl chloride or phenyl chlorosulphinate was used. In the same manner, the reaction of phenol with symmetrical dialkyl sulphoxides, e.g. (**1b**), (**1c**), and (**1d**), gave the expected *ortho*-alkylphenols in good yields (Table 1). Although the reaction between phenol and DMSO (**1a**) gave a small amount of 2,6-bis(methylthiomethyl)phenol as a by-product, the use of these sulphoxides gave no disubstituted phenols because of the steric hindrance of the *ortho*-alkylphenols formed.

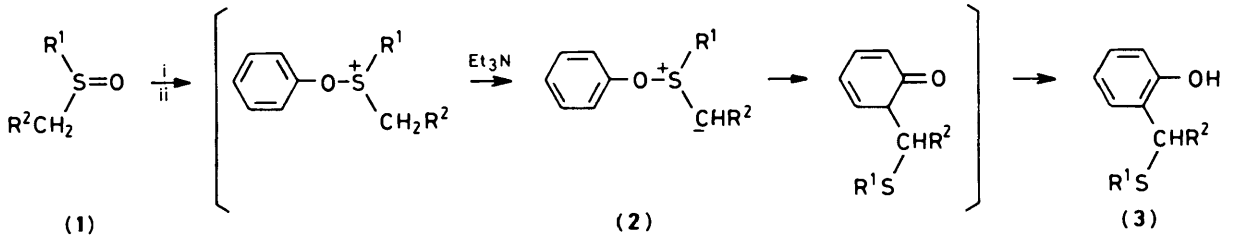
For the reaction of phenol with aryl alkyl sulphoxides, the reaction was affected by the type of alkyl group. The reaction of phenol with methyl phenyl sulphoxide (**1e**) gave *o*-phenylthiomethylphenol (**3e**) in good yields. However phenol failed to react with ethyl phenyl sulphoxide (**1f**) or chloromethyl phenyl sulphoxide, unchanged starting material being recovered. When diallyl sulphoxide (**1g**) or ethyl methylsulphinylacetate (**1h**) was used as the sulphoxide, no alkylation of phenol took place. In these cases the sulphoxide (**1g**) and (**1h**) did indeed react with the activator and the formation of the sulphonium ylides was evidenced by the appearance of red colour in the reaction solution. Therefore, the decrease of nucleophilicity of the ylides, (**2g**) and (**2h**), through delocalization appears to make the [2,3]-sigmatropic rearrangement very difficult.

It is thought that salicylaldehyde (**6**) can be prepared by

**Table 1.** Reaction of phenol and various sulphoxides (**1**)

| Sulphoxide | $R^1$ | $R^2$ | Product | Yield (%) Method A[a] | Yield (%) Method B[b] |
|---|---|---|---|---|---|
| (**1a**) | Me | H | (**3a**) | 57 | 78 |
| (**1b**) | $CH_2Me$ | Me | (**3b**) | 67 | 69 |
| (**1c**) | $CH_2Ph$ | Ph | (**3c**) | 75 | 68 |
| (**1d**) | $(CH_2)_3Cl$ | $(CH_2)_2Cl$ | (**3d**) | —[c] | 61 |
| (**1e**) | Ph | H | (**3e**) | 76 | 65 |

[a] Method A: phenyl chlorosulphinate was used for this procedure. [b] Method B: thionyl chloride was used as an activator of sulphoxides. [c] This reaction was not investigated.

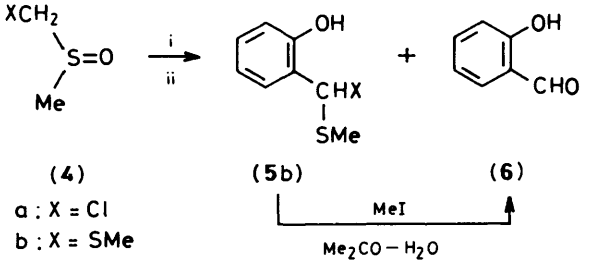



**a**; $R^1$ = Me $R^2$ = H
**b**; $R^1$ = $CH_2Me$ $R^2$ = Me
**c**; $R^1$ = $CH_2Ph$ $R^2$ = Ph
**d**; $R^1$ = $CH_2CH_2CH_2Cl$ $R^2$ = $CH_2CH_2Cl$
**e**; $R^1$ = Ph $R^2$ = H
**f**; $R^1$ = Ph $R^2$ = $CH_3$
**g**; $R^1$ = $CH_2CH{=}CH_2$ $R^2$ = $CH{=}CH_2$
**h**; $R^1$ = $CH_3$ $R^2$ = $CO_2Et$

**Scheme 1.** *Reagents:* i, $SOCl_2$ or $ClSO_2Ph$; ii, PhOH

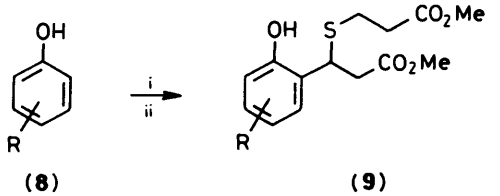
*ortho*-selective formylation of phenol. Therefore, we investigated the synthesis of 2-[chloro(methylthio)methyl]phenol and 2-bis(methylthio)methylphenol, as analogues of salicylaldehyde (**6**). These derivatives could be expected to form on alkylation of the phenol with chloromethyl methyl sulphoxide (**4a**) or methyl methylthiomethyl sulphoxide (FAMSO; **4b**) by the present procedure.

The sulphoxide (**4a**) in combination with thionyl chloride or phenyl chlorosulphinate afforded salicylaldehyde (**6**) directly in 13 or 29% yields, respectively. When FAMSO (**4b**) and phenyl chlorosulphinate were used as starting materials, the expected dithioacetal (**5b**) and salicylaldehyde (**6**) were obtained in 26 and 27% yields, respectively. Since the resulting dithioacetal (**5b**) underwent hydrolysis when treated with methyl iodide in acetone–water under reflux for 4 h, giving salicylaldehyde in 75% yield (Scheme 2), the total yield of salicylaldehyde (**6**) amounted to 46% with this procedure. However, the use of thionyl chloride instead if phenyl chlorosulphinate resulted in a very complicated mixture of products from which the dithioacetal (**5b**) and the aldehyde (**6**) were absent.




**Scheme 2.** *Reagents:* i, $SOCl_2$ or $ClSO_2Ph$; ii, PhOH

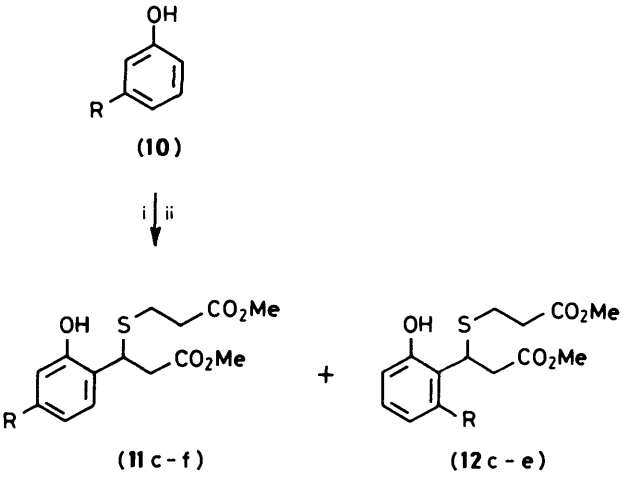
Next, the synthesis of coumarins was investigated by the reaction between phenols and dimethyl 3,3′-sulphinyldipropionate (**7**), followed by the cyclization of alkylated phenols thus formed. The reaction of phenol with compound (**7**) using thionyl chloride as the activating agent followed by treatment with triethylamine afforded dimethyl 3-(2-hydroxyphenyl)-3,3′-thiodipropionate (**9a**) in 84% yield. The *ortho*- or *para*-substituted phenols (**8b**—**m**) also underwent alkylation similarly in moderate to good yields, except in the case of *o*-chlorophenol (**8d**) and methyl *p*-hydroxybenzoate (**8l**) (Scheme 3, Table 2). When (**8d**) was used for this reaction, compound (**9a**) was produced as a by-product and the expected product (**9d**) was obtained in only 19% yield. The reaction of (**8l**) gave the single product (**9l**) in low yield because of the very limited solubility of (**8l**) in dichloromethane at low temperature.




**a**; R = H
**b**; R = 2-Me
**c**; R = 2-OMe
**d**; R = 2-Cl
**e**; R = 2-OAc
**f**; R = 2-$CO_2$Me
**g**; R = 2-$NO_2$
**h**: R = 4-Me
**i**; R = 4-Me
**j**; R = 4-Cl
**k**; R = 4-OAc
**l**; R = 4-$CO_2$Me
**m**; R = 4-$NO_2$

**Scheme 3.** *Reagents:* i, $O{=}S(CH_2CH_2CO_2Me)_2$ (**7**), $SOCl_2$; ii, $Et_3N$

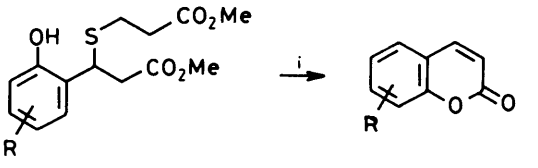
The reaction of *meta*-substituted phenols (**10**) with sulphoxide (**7**) was affected by the nature of the phenol substituents and afforded a mixture of two possible rearrangement products (Scheme 4, Table 3). None of the expected products were obtained with phenols having electron-donating groups such as OH, OMe, and Me, whereas in the case of other *meta*-substituted phenols (**10c**—**e**) a mixture of the *o*-alkylated phenols (**11**) and (**12**) was afforded in moderate yields. It is noteworthy that *m*-nitrophenol (**10f**) produced a single substitution product (**11f**) in a low yield. This result seems to come from the intensive electron-withdrawing nature of the nitro group.




**a**; R = Me
**b**; R = OMe
**c**; R = Cl
**d**; R = OAc
**e**; R = $CO_2$Me
**f**; R = $NO_2$
**g**; R = OH

**Scheme 4.** *Reagents:* i, (**7**), $SOCl_2$; ii, $Et_3N$

Dimethyl 3-(2-hydroxyphenyl)-3,3′-thiodipropionate (**9a**) was treated with potassium carbonate in acetone under reflux to give the coumarin (**13a**) in 83% yield (Scheme 5). The other rearrangement products (**9b**—**l**) and (**11e**) were cyclized to give the substituted coumarins (**13b**—**m**) in good yields, except in the case of (**9f**), (**9g**) and (**9l**) (Table 4). In these cases the resulting phenoxide anion was unable to attack the carbonyl group of the propionic acid moiety because of the decrease in its nucleophilicity by these substituents. The acetoxy group of (**9e**) and (**9k**) was hydrolysed under these reaction conditions, giving the corresponding hydroxycoumarins (**13e**) and (**13k**), respectively.




**a**; R = H
**b**; R = 8-Me
**c**; R = 8-OMe
**d**: R = 8-Cl
**e**; R = 8-OH
**h**; R = 6-Me
**i**; R = 6-OMe
**j**; R = 6-Cl
**k**; R = 6-OH
**m**; R = 7-$CO_2$Me

**Scheme 5.** *Reagent:* i, $K_2CO_3$

**Table 2.** Reaction of *ortho*- and *para*-substituted phenols and dimethyl 3,3′-sulphinyldipropionate (**7**) using thionyl chloride

| Phenol | R | Product | Yield (%) | $\nu_{max.}$/cm$^{-1}$ | $^1$H N.m.r. (δ, *J* in Hz; $CCl_4$ or $CDCl_3$) |
|---|---|---|---|---|---|
| (**8a**) | H | (**9a**) | 84 | 3 400, 1 735, 1 240 | 2.53 (4 H, m), 2.85 (2 H, d, *J* 7), 3.65 (6 H, s), 4.63 (1 H, t, *J* 7), 6.7—7.4 (5 H, m) |
| (**8b**) | 2-Me | (**9b**) | 53 | 3 450, 1 715, 1 220 | 2.23 (3 H, s), 2.50 (4 H, m), 2.83 (2 H, d, *J* 8), 3.63 (3 H, s), 3.67 (3 H, s), 4.53 (1 H, t, *J* 8), 6.6—7.2 (4 H, m) |
| (**8c**) | 2-OMe[a] | (**9c**) | 42 | 3 450, 1 715, 1 275, 1 215 | 2.57 (4 H, m), 2.85 (2 H, d, *J* 7), 3.63 (6 H, s), 3.87 (3 H, s), 4.73 (1 H, t, *J* 7), 6.10 (1 H, m), 6.6—7.1 (3 H, m) |
| (**8d**) | 2-Cl[b] | (**9d**) | 19 | 3 450, 1 720, 1 250 | 2.58 (4 H, m), 2.83 (2 H, d, *J* 8), 3.63 (6 H, s), 4.70 (1 H, t, *J* 8), 6.6—7.3 (4 H, m) |
| (**8e**) | 2-OAc | (**9e**) | 60 | 3 400, 1 730, 1 210 | 2.22 (3 H, s), 2.57 (4 H, m), 2.87 (2 H, d, *J* 7), 3.60 (6 H, s), 4.72 (1 H, *J* 7), 6.6—7.3 (4 H, m) |
| (**8f**) | 2-$CO_2$Me | (**9f**) | 41 | 3 100, 1 720, 1 275 | 2.60 (3 H, s), 2.83 (2 H, d, *J* 8), 3.63 (6 H, s), 3.97 (3 H, s), 4.73 (1 H, t, *J* 8), 6.83 (1 H, d, *J* 8), 7.60 (1 H, d, *J* 8), 7.73 (1 H, d, *J* 8), 11.13 (1 H, s) |
| (**8g**) | 2-$NO_2$[c] | (**9g**) | 53 | 3 220, 1 735, 1 250 | 2.62 (4 H, m), 2.87 (2 H, d, *J* 7), 3.63 (6 H, s), 4.73 (1 H, t, *J* 7), 6.97 (1 H, t, *J* 8), 7.73 (1 H, d, *J* 8), 8.03 (1 H, d, *J* 8), 11.16 (1 H, s) |
| (**8h**) | 4-Me | (**9h**) | 70 | 3 400, 1 720, 1 250 | 2.27 (3 H, s), 2.53 (4 H, m), 2.82 (2 H, d, *J* 7), 3.63 (6 H, s), 4.53 (1 H, t, *J* 7), 6.5—7.2 (4 H, m) |
| (**8i**) | 4-OMe | (**9i**) | 39 | 3 420, 1 740, 1 250, 1 210 | 2.57 (4 H, m), 2.83 (2 H, d, *J* 8), 3.60 (6 H, s), 3.70 (3 H, s), 4.67 (1 H, t, *J* 8), 6.4—6.9 (4 H, m) |
| (**8j**) | 4-Cl | (**9j**) | 30 | 3 400, 1 715, 1 240 | 2.60 (4 H, m), 2.85 (2 H, d, *J* 8), 3.67 (6 H, s), 4.67 (1 H, t, *J* 8), 6.73 (1 H, d, *J* 8), 7.05 (1 H, dd, *J* 2 and 8), 7.28 (1 H, d, *J* 2), 7.60 (1 H, br s) |
| (**8k**) | 4-OAc[d] | (**9k**) | 77 | 3 400, 1 730, 1 200 | 2.20 (3 H, s), 2.53 (4 H, m), 2.80 (2 H, d, *J* 7), 3.57 (6 H, s), 4.60 (1 H, t, *J* 7), 6.6—7.0 (3 H, m), 7.27 (1 H, m) |
| (**8l**) | 4-$CO_2$Me | (**9l**) | 13 | 3 350, 1 735, 1 720, 1 285, 1 250 | 2.57 (4 H, m), 2.87 (2 H, d, *J* 8), 3.67 (6 H, s), 3.87 (3 H, s), 4.67 (1 H, t, *J* 8), 6.83 (1 H, d, *J* 8), 7.75 (1 H, dd, *J* 2 and 8), 7.93 (1 H, d, *J* 2), 7.5—8.2 (1 H, m) |
| (**8m**) | 4-$NO_2$ | (**9m**) | 45 | 3 220, 1 750, 1 250 | 2.70 (4 H, m), 3.02 (2 H, d, *J* 8), 3.72 (6 H, s), 4.78 (1 H, t, *J* 8), 6.98 (1 H, d, *J* 8), 8.03 (1 H, dd, *J* 2 and 8), 8.32 (1 H, d, *J* 2), 7.7—8.5 (1 H, m) |

[a] Dimethyl 3-(2-methoxyphenoxy)-3,3′-thiodipropionate was obtained in 5% yield. [b] Compound (**9a**) and 2,6-bis{2-(methoxycarbonyl)-1-[2-(methoxycarbonyl)ethylthio]ethyl}phenol were obtained in 13 and 3% yield, respectively. [c] Dimethyl 3-(2-nitrophenoxy)-3,3′-thiodipropionate was obtained in 5% yield. [d] Disubstituted product of (**8k**) was obtained in 4% yield.

**Table 3.** Reaction of *m*-substituted phenols and dimethyl 3,3′-sulphinyldipropionate (**7**) using thionyl chloride

| | | Product | | | |
|---|---|---|---|---|---|
| Phenol | R | | Yield (%) | | Yield (%) |
| (**10c**) | Cl[a] | (**11c**) | 3 | (**12c**) | 3 |
| (**10d**) | OAc[a] | (**11d**) | 23 | (**12d**) | 23 |
| (**10e**) | $CO_2$Me | (**11e**) | 20[b] | (**12e**) | 22[b] |
| (**10f**) | $No_2$[c] | (**11f**) | 7 | (**12f**) | 0 |

[a] The yield of the isomers were determined by $^1$H n.m.r. integration of the mixture. [b] Yield based on pure isolated products. [c] Dimethyl 3-(3-nitrophenoxy)-3,3′-thiodipropionate was obtained in 4% yield.

**Table 4.** Preparation of coumarins

| Coumarin | R | Yield (%) | M.p. (°C) (lit. ref.) |
|---|---|---|---|
| (**13a**) | H | 83 | 68—69 (70.2—70.6)[2] |
| (**13b**) | 8-Me | 89 | 110—111 (111.5)[3] |
| (**13c**) | 8-OMe | 92 | 86—88 (89—90)[4] |
| (**13d**) | 8-Cl | 68 | 151—153 (146—147)[5] |
| (**13e**) | 8-OH | 93 | 161.5 (160)[6] |
| (**13h**) | 6-Me | 92 | 73—74 (72)[7] |
| (**13i**) | 6-OMe | 96 | 103—104 (103—104)[8] |
| (**13j**) | 6-Cl | 73 | 170—171 (164)[9] |
| (**13k**) | 6-OH | 94 | 241 (249—250)[6] |
| (**13m**) | 7-$CO_2$Me | 40 | 172—175 — |

**Table 5.** Physical properties of the rearrangement products

| Compd. | I.r.($\nu_{max.}$/cm$^{-1}$) | $^1$H N.m.r. (δ, *J* in Hz; $CDCl_3$) |
|---|---|---|
| (**3b**) | 3 270 | 1.15 (3 H, t, *J* 7.5), 1.56 (3 H, d, *J* 7.5), 2.31 (2 H, q, *J* 7.5), 4.14 (1 H, q, *J* 7.5), 6.5—7.3 (5 H, m) |
| (**3c**) | 3 300 | 3.53 (2 H, s), 5.10 (1 H, s), 6.6—7.5 (15 H, m) |
| (**3d**) | 3 300, 1 590, 1 460, 1 230 | 1.90 (2 H, quintet, *J* 6), 2.25 (2 H, q, *J* 6), 2.50 (2 H, t, *J* 6), 3.47 (4 H, t, *J* 6), 4.23 (1 H, t, *J* 8), 6.3—7.3 (5 H, m) |
| (**3e**) | 3 400 | 4.15 (2 H, s), 6.10 (1 H, s), 6.6—7.5 (9 H, m) |
| (**5b**) | 3 370 | 2.11 ( 6 H, s), 5.06 (1 H, s), 6.8—7.4 (5 H, m) |
| (**11c**) + (**12c**) | 3 380, 1 725, 1 250 | 2.5—2.7 (4 H, m), 2.78, 2.97 (2 H, d, *J* 8), 3.67 (6 H, s), 4.63, 5.13 (1 H, t, *J* 8), 6.8—7.4 (4 H, m), 7.73 (1 H, m) |
| (**11d**) + (**12d**) | 3 400, 1 735, 1 240, 1 210 | 2.20, 2.30 (3 H, s), 2.53 (4 H, m), 2.83, 2.87 (2 H, d, *J* 8), 3.63 (6 H, s), 4.63, 4.74 (1 H, t, *J* 8), 6.5—7.6 (4 H, m) |
| (**11e**) | 3 370, 1 715, 1 285, 1 245 | 2.63 (4 H, m), 2.93 (2 H, d, *J* 6), 3.53 (3 H, s), 3.57 (3 H, s), 3.83 (3 H, s), 5.28 (1 H, t, *J* 6), 6.8—7.2 (3 H, m), 7.5—8.1 (1 H, m) |
| (**12e**) | 3 400, 1 725, 1 295, 1 235 | 2.57 (4 H, m), 2.87 (2 H, d, *J* 8), 3.60 (6 H, s), 3.83 (3 H, s), 4.70 (1 J, t, *J* 8), 7.1—7.7 (4 H, m) |
| (**11f**) | 3 320, 1 730, 1 260 | 2.67 (4 H, m), 3.00 (2 H, d, *J* 8), 3.70 (6 H, s), 4.80 (1 H, t, *J* 8), 7.2—8.0 (4 H, m) |

## Experimental

M.p.s are uncorrected. I.r. spectra were measured on either a Hitachi 215 or a Hitachi 260-50 spectrometer. $^1$H N.m.r. spectra were obtained with JEOL JNM-C-60M or JEOL FT-90Q spectrometers using tetramethylsilane as an internal standard. Column chromatography was carried out with Wakogel C-200 (Wako Pure Chemical Industries). Spectral data are summarised in Tables 2 and 5.

*General Procedure for the* o-*Alkylation of Phenol Using Phenyl Chlorosulphinate.*—The sulphoxide [*e.g.* (**1**) or (**4**)] (4.2

mmol) was added dropwise to a solution of phenyl chlorosulphinate (705 mg, 4.0 mmol) in dry dichloromethane (15 ml) maintained at −55 °C for 5 min under a dry nitrogen atmosphere. After the mixture had been stirred for 45 min at −55 to −50 °C, the phenol (1.0 g, 10.6 mmol) was added, followed by triethylamine (3 ml) in dry dichloromethane (3 ml) at −50 °C. The solution was allowed to warm to room temperature and the reaction mixture was poured into dilute hydrochloric acid. The organic layer was separated, and the aqueous solution was extracted with diethyl ether (2 × 20 ml). The combined organic layers were washed with water and then brine, dried ($MgSO_4$), and evaporated, and the residual oil was chromatographed on a column (5% ethylacetate–hexane) to give the *o*-alkylated phenol [*e.g.* (**5**) or (**7b**)] or salicylaldehyde (**6**).

*General Procedure for* o-*Alkylation of Phenols Using Thionyl Chloride*.—Thionyl chloride (0.35 ml, 4.8 mmol) in dry dichloromethane (5 ml) was added dropwise to a solution of the sulphoxide [*e.g.* (**1**), (**4**), or (7)] (4.0 mmol) in dry dichloromethane (10 ml) at −60 °C for 3 min under a dry nitrogen atmosphere, and the mixture was stirred for 15 min. To the solution was gradually added the phenol [*e.g.* (**8**) or (**10**)] (16 mmol) in dry dichloromethane (5 ml) at −55 °C for 10 min. After the mixture had been stirred for 1 h, triethylamine (2.5 ml) in dry dichloromethane (2 ml) was added to the reaction mixture at −50 °C. The solution was allowed to warm to room temperature, and was then poured into dilute hydrochloric acid. The organic layer was separated and the aqueous solution was extracted with diethyl ether (2 × 20 ml). The combined organic layers were washed with water and brine, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed on a column (5% ethyl acetate–hexane) to give the *o*-alkylated phenol [*e.g.* (**3**), (**9**), (**11**) or (**12**)] or salicylaldehyde (**6**).

*Hydrolysis of the Dithioacetal* (**5b**).—Iodomethane (1.1. g, 7.7 mmol) was added to a solution of dithioacetal (**5b**) (206 mg, 1.0 mmol) in acetone (10 ml) containing a small amount of water at room temperature. The mixture was refluxed for 7 h, concentrated, diluted with water and the solution extracted with diethyl ether (50 ml). The organic layer was washed with water and brine, dried ($MgSO_4$), and then evaporated. The residue was chromatographed on a column (40% dichloromethane–hexane) to afforded salicylaldehyde (**6**) (92 mg, 75%).

*Preparation of the Coumarin* (**13**).—Anhydrous potassium carbonate (1.38 g, 10 mmol) was added to a solution of the rearrangement product [e.g. (**9**) or (**11e**)] (1.0 mmol) in acetone (10 ml). The reaction mixture was refluxed for 1.5 h, after which the potassium carbonate was filtered off, and the filtrate evaporated. The resulting mixture was chromatographed on a column (benzene) to afford the coumarin (**13**).

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