Table I. Oxidative Decarboxylation of Phenylacetic Acids

| R = [a] | Aldehyde, %[b] | Kolbe dimer, %[c] | Other products, %[d] |
|---|---|---|---|
| 4-Methoxy | 72 | | 4-Methoxybenzoic acid, 14% |
| 3-Methoxy | 78 | | 3-Methoxybenzoic acid, 12% |
| 4-Chloro | 62 | 12 | 4-Chlororbenzoic acid, 15% |
| Hydrogen | 41 | 52 | |
| 4-Nitro | 0 | 82 | |

[a] Registry no. are, respectively, 104-01-8, 1798-09-0, 1878-66-6, 103-82-2, 104-03-0. [b] Registry no. are, respectively, 123-11-5, 591-31-1, 104-88-1, 100-52-7. [c] Registry no. are, respectively, 5216-35-3, 103-29-7, 736-30-1. [d] Registry no. are, respectively, 100-09-4, 586-38-9, 74-11-3.

taining a gas lead in pipe and condenser, and, in the outer joints, a pair of smooth platinum electrodes (1 $cm^2$). The electrodes were placed parallel to each other 3 cm apart.

**4-Methoxybenzaldehyde.** To a solution of 3.32 g (0.02 mol) of 4-methoxyphenylacetic acid in 70 ml of dry $Me_2SO$ was added 0.48 g (0.01 mol) of 50% sodium hydride suspended in mineral oil. This solution was placed in the above cell. The solution was degassed by bubbling nitrogen through the stirred solution for 30 min. Fifty-five volts at 0.25 A was applied to the solution for 4 h. Sodium bicarbonate (5 g, 0.065 mol) was added and the mixture heated to 150 °C for 4 min and cooled rapidly by quenching in an ice bath. The mixture was poured into 350 ml of saturated sodium chloride solution. This was extracted with 4 × 150 ml of ether. Evaporation of the solvent left an oily residue which, on distillation, afforded 1.96 g (74%) of 4-methoxybenzaldehyde. The physical and spectral properties were identical with those of an authentic sample.

The aqueous layer was acidified and extracted with 3 × 75 ml of ether. On evaporation of the solvent a crystalline solid remained which was recrystallized to afford 0.44 g (14%) of 4-methoxybenzoic acid.

The reaction was repeated with the following phenylacetic acids: 3-methoxy, 4-chloro, hydrogen, and 4-nitro. The results are given in Table I. All products were identified by comparison with authentic samples.

## References and Notes


(1) N. L. Weinberg, Ed., "Technique of Electroorganic Synthesis", Part I, Wiley, New York, N.Y., 1974, Chapter VI, p 793.
(2) J. P. Coleman, J. H. P. Utley, and B. C. L. Weedon, *Chem. Commun.*, 438 (1971); J. P. Coleman, R. Lines, J. H. P. Utley, and B. C. Weedon, *J. Chem. Soc., Perkin Trans. 2*, 1064 (1974).
(3) S. Torii, T. Okamoto, G. Tanida, H. Hino, and Y. Kitsuya, *J. Org. Chem.*, **41**, 166 (1976).
(4) K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **85**, 3027 (1963); **87**, 5661, 5670 (1965).


## Preparation of Alkyl Phenyl Sulfides by Electrophilically Catalyzed Displacement of Certain Nucleophiles by Thiophenoxy Group[1]


Maria Micha-Screttas and Constantinos G. Screttas*

*The National Hellenic Research Foundation, Athens 501/1, Greece*


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Water and alcohols are commonly considered to be solvents of high nucleophilicity[2] and upon their reaction with a carbenium ion afford the corresponding alcohol and ether. In fact, Winstein et al.[3] have employed water as an effective agent for intercepting carbocationic species in order to elucidate relevant reaction mechanisms. More recently certain charged nucleophiles, such as azide ion, have been used for the same purpose.[4] Comparing Ritchie's $N_+$ values for various *charged* nucleophiles, it appears that thiophenoxide anion is by far a better trapping agent than azide by over two orders of magnitude in methanol and even larger in $Me_2SO$.[4] $N_+$ values for a given nucleophile show a marked dependence upon the medium, the obvious trend being the greater the basicity of the medium the larger the $N_+$ value. In a protic medium of high acidity thiophenoxide can no longer exist, of course, as a charged species but rather as its protonated form, namely thiophenol. The purpose of this note is to show that thiophenol itself exhibits a marked reactivity toward carbenium ions, being capable of displacing rather readily various nucleophiles at a carbenium ion center (eq 1).

$$RZ + PhSH \xrightarrow{cat.} RSPh + HZ \quad (1)$$
$$Z = OH, OR, Cl, N_3$$

The ready conversion of triphenylcarbinol and *tert*-butyl alcohol to the corresponding alkyl sulfides by their acid-catalyzed reaction with thiols[5] has been known for a long time. It is quite probable that this reaction owes its feasibility to the ready ionization of these alcohols in acid media, and to the pronounced nucleophilicity of thiols. Employing a modification of this method we found that certain alkyl phenyl sulfides can be prepared very conveniently and in high yields. The results are summarized in Table I. According to this method an alcohol is transformed to the corresponding alkyl phenyl sulfide by boiling an equimolar mixture of the alcohol and thiophenol in benzene or methylcyclohexane, in the presence of perchloric acid catalyst. The results indicate that ease of reaction and product yield are highly dependent on the structure of the alcohol. Aryl methanols and tertiary alcohols, which are expected to have high $pK_{R^+}$ values, react readily with thiophenol and the yields of the sulfides are usually good to excellent. Primary alcohols require exceedingly long reaction times and even so the corresponding sulfides are produced in very poor yields.

Perhaps more novel could be the ready displacement of alcohol in the acid-catalyzed reaction between thiophenol and certain ethers. Upon dissolving an equimolar mixture of 2-phenylisopropyl methyl ether and thiophenol in trifluoroacetic acid (TFA) an exothermic reaction takes place and the ether is transformed instantly into the relevant phenyl sulfide (eq 2).

$$Ph(CH_3)_2COCH_3 + PhSH \xrightarrow{TFA} Ph(CH_3)_2CSPh + CH_3OH \quad (2)$$

Results with various ethers from reactions such as 2 are summarized in Table II. Two main factors seem to emerge from the examination of the data. (a) The basicity of the ether; comparing cases 2 and 3 it can be seen that methyl ether is less reactive than the ethyl analogue, and this might well be due to lower basicity of the methyl ether[6] (eq 3a). (b) The stability

$$ArCH_2{-}OR + H^+ \rightleftharpoons ArCH_2{-}O^+(H)H \quad (a)$$
$$ArCH_2{-}O^+(H)H \rightleftharpoons ArCH_2^+ + ROH \quad (b) \quad (3)$$

of the carbenium ion produced in step b obviously is the second important factor. *o*-Chlorobenzyl methyl ether appears to be inert under the reaction conditions employed in this investigation, whereas the *p*-chlorobenzyl ether reacted incompletely. This can be understood by comparing, for example, the ionization potentials of benzyl and *p*-chlorobenzyl radicals.[8] *p*-Chlorobenzyl cation appears to be less stable by

**Table I**

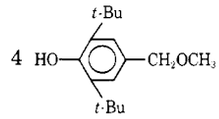
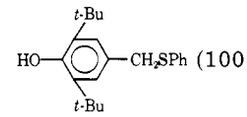
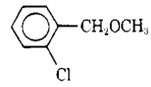
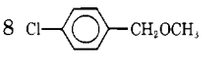
$$ROH + PhSH \xrightarrow[-H_2O]{H^+ClO_4^-} RSPh$$

| Registry no. | Alcohol | Reaction time | Sulfide (yield, %) | Registry no. |
|---|---|---|---|---|
| 100-51-6 | $PhCH_2OH$[a] | 16 min | $PhCH_2SPh$ (25) | 831-91-4 |
| 105-13-5 | $p$-$CH_3OC_6H_4CH_2OH$[b] | 15 min | $p$-$CH_3OC_6H_4CH_2SPh$ (90) | 5023-67-6 |
| 98-85-1 | $Ph(CH_3)CHOH$[b] | 15 min | $Ph(CH_3)CHSPh$ (100) | 21213-26-3 |
| 91-01-0 | $Ph_2CHOH$[b] | 11 min | $Ph_2CHSPh$ (100) | 21122-20-3 |
| 75-84-3 | $(CH_3)_2(CH_3CH_2)COH$[b] | 30 min | $(CH_3)_2(CH_3CH_2)CSPh$ (53) | 41469-79-8 |
| 123-51-3 | $(CH_3)_2CHCH_2CH_2OH$[c] | 84 h | $(CH_3)_2CHCH_2CH_2SPh$ (13) | 13910-11-7 |

[a] In boiling methylcyclohexane. [b] In boiling benzene. [c] In boiling toluene. Standard conditions: 0.1 mol alcohol; 0.1 mol PhSH; 1.0 mL 70% $H^+ClO_4^-$; solvent 100 mL; Dean-Stark water separator.

**Table II**

$$R\text{-}OR' + PhSH \xrightarrow{TFA} R\text{-}SPh + R{-}OH$$

| Registry no. | Ether | Remarks | Sulfide (conversion,[a] %) | Registry no. |
|---|---|---|---|---|
| 935-67-1 | 1 $Ph(CH_3)_2COCH_3$ | Rapid, RT[b] | $Ph(CH_3)_2CSPh$ (100) | 4148-93-0 |
| 538-86-3 | 2 $PhCH_2OCH_3$ | 24 h, 53 °C, incomplete reaction | $PhCH_2SPh$ (75) | |
| 539-30-0 | 3 $PhCH_2OCH_2CH_3$ | 24 h, 53 °C, complete reaction | $PhCH_2SPh$ (100) | |
| 87-97-8 | 4  | Rapid, RT |  (100) | 17258-84-3 |
| 5670-78-0 | 5 $Ph_2CHOCH_2CH_3$ | Very rapid, RT | $Ph_2CHSPh$ (100) | |
| 7495-83-2 | 6 $Ph_2CHO(CH_2)_3CH_3$ | Very rapid, RT | $Ph_2CHSPh$ (100) | |
| 59579-08-7 | 7  | No reaction, 53 °C, 48 h | | |
| 1195-44-8 | 8  | 61 h, 53 °C, incomplete reaction | $p$-$ClC_6H_4CH_2SPh$ (70) | 7693-30-3 |
| 10574-17-1 | 9 $PhOCH(CH_2CH_3)CH_3$ | No reaction, 48 h, 53 °C | | |
| 103-50-4 | 10 $PhCH_2OCH_2Ph$ | 42 h, 53 °C, complete reaction | $PhCH_2SPh$ (100) | |

[a] Based on analysis by NMR. [b] Standard conditions: 10 mmol of ether, 15 mmol of thiophenol, 2 mL of TFA.

4 kcal/mol. An even larger[9] destabilizing effect could be expected for the $o$-chloro substituent.

The transformation depicted in eq 4 has been carried out successfully.

$$ROR' + HN_3 \xrightarrow{TFA} RN_3 + R'OH$$

$$RN_3 + PhSH \xrightarrow{TFA} RSPh + HN_3 \quad (4)$$

R = 2-phenylisopropyl, benzhydryl, 3,5-di-*tert*-butyl-4-hydroxybenzyl

The ease of reaction of the azides studied seems to parallel that of the corresponding ethers. For example, 2-phenylisopropyl azide reacts exothermically with thiophenol in the presence of TFA and it is converted to the relevant sulfide rapidly. It is quite possible that the displacement of the azide group follows an $S_N1$ pathway, through the intermediacy of a protonated azide species (eq 5).

$$RN_3 \xrightarrow{TFA} RN_3{}^+H \rightarrow R^+ + HN_3 \xrightarrow{PhSH} RSPh \quad (5)$$

Certain organic halides were found to react with thiophenol in $POCl_3$ solvent and in the presence of catalytic amounts of ferric chloride (eq 6).

$$RCl + PhSH \xrightarrow[POCl_3]{FeCl_3} RSPh + HCl \quad (6)$$

Particularly clean reaction occurs with *tert*-butyl chloride and the yield of the *tert*-butyl phenyl sulfide is quantitative. Less reactive appears to be benzyl chloride; under the same conditions about 30% remained unreacted. Employing ferric chloride and *tert*-butyl chloride in equimolar quantities the reaction with thiophenol is complete within minutes at room temperature. This most probably means that under these conditions *tert*-butyl chloride ionizes to the relevant carbenium ion to a substantial extent[11] (eq 7).

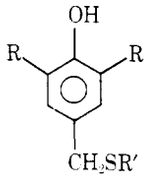
$$t\text{-}BuCl + FeCl_3 \xrightarrow{POCl_3} t\text{-}Bu^+FeCl_4^-$$

$$\xrightarrow[fast]{PhSH} t\text{-}BuSPh + H^+FeCl_4^- \quad (7)$$

The chlorides *n*-butyl, *sec*-butyl, benzhydryl, and *p*-chlorobenzyl did not react with thiophenol in $POCl_3$ and in the presence of catalytic amount of ferric chloride. Antimony pentachloride in $POCl_3$ did not catalyze the reaction of *sec*-butyl chloride with thiophenol.

Benzhydryl benzoate (BB) undergoes ready solvolysis by thiophenol in TFA and affords the corresponding sulfide quantitatively. However, when thiophenol is allowed to compete against ethanol for a limited amount of BB in TFA the sulfide, which is the sole reaction product, is produced at a very slow rate, incomplete reaction in 12 h at 53 °C vs. a few seconds at room temperature, in the presence and in absence of ethanol, respectively. This finding probably indicates that esters could be more susceptible to acid catalysis in their solvolysis with thiols rather than with alcohols. Specific interaction of the acid catalyst with alcohol, manifested, for example, as a leveling effect, could be responsible for this phenomenon.

It is felt that the chemistry described in this note could be of a wider synthetic utility. The ready availability of methyl ethers by methoxymethylation[13] of hindered phenols in conjunction with their ready reaction with thiophenol, and most probably with other thiols, could make the sulfides of the general structure A readily available.




A

## Experimental Section

*p*-Methoxybenzyl alcohol was prepared by sodium borohydride reduction of anisaldehyde (Fluka). The other alcohols used in this work were products of Merck. Methyl and ethyl benzyl ethers as well as chlorobenzyl methyl ethers were prepared by the classic Williamson synthesis from the corresponding benzyl chlorides. Ethyl and butyl benzhydryl ethers were prepared according to a procedure of "Organic Syntheses".[14] Dibenzyl ether was purchased from Fluka. 3,5-Di-*tert*-butyl-4-hydroxybenzyl methyl ether[13] and 2-phenylisopropyl methyl ether[15] were prepared according to the literature. *sec*-Butyl phenyl ether and benzhydryl benzoate were prepared as described in this section.

The following preparation serves as an example for the transformation of an alcohol to the corresponding phenyl sulfide.

**1-Phenylethyl Phenyl Sulfide.** The reaction system was a 500-mL Erlenmeyer flask with ground joint, equipped with a magnetic stirring bar, a Dean-Stark water separator, and a reflux condensor. A stirred mixture of 12.2 g (0.1 mol) of 1-phenylethanol, 11 mL of thiophenol, 100 mL of dry benzene, and 1.0 mL of 70% perchloric acid was heated rapidly to reflux. In 5.5-min time from the beginning of reflux 1.0 mL of water had been collected. At 6.0 min the solution turned pale yellow. At 8.5 min, 1.5 mL of water had been separated; at this stage the solution was bright yellow. At 10.5 min the solution turned brown-red. Sodium hydroxide solution (10%, 50 mL) was added to the reaction mixture, and after stirring for a few minutes the benzene layer was separated, washed with water, dried over anhydrous magnesium sulfate, and evaporated to smallest volume in the rotary evaporator. The free of benzene liquid portion weighed 21.5 g and was found to be 1-phenylethyl phenyl sulfide by NMR analysis in a better than 95% purity, yield quantitative.

***sec*-Butyl Phenyl Ether.** A mixture of 30 g of anhydrous potassium carbonate, 23.5 g (0.25 mol) of phenol, and 45 mL of *sec*-butyl bromide in 100 mL of diethylene glycol was stirred and heated for about 2 h, so that the excess of bromide was refluxing gently. During this period of time the following changes were observed. Firstly, $K_2CO_3$ dissolved, then a white precipitate formed, and finally the mixture started foaming. At this stage the reaction mixture was poured into 500 mL of water. The upper layer was separated, diluted with benzene (150 mL), washed with sodium hydroxide solution and then with water, and dried over $MgSO_4$. The product, after removal of the solvent, was subjected to vacuum distillation. The fraction boiling (3.5 mm) at 59–60 °C weighed 26.7 g (71%), based on phenol used, and it was *sec*-butyl phenyl ether (NMR).

**3,5-Di-*tert*-butyl-4-hydroxybenzyl Phenyl Sulfide.** 3,5-Di-*tert*-butyl-4-hydroxybenzyl methyl ether (1.25 g, 5 mmol) was dissolved in 2 mL of thiophenol with development of a yellow coloration. Addition of 0.25 mL of 70% perchloric acid caused a mild exotherm and the solution was decolorized instantly. The resulting mixture was shaken for a few seconds and then allowed to stand at room temperature for 15 h. Excess thiophenol was removed from the product by steam distillation, the nonvolatile product was taken up in ether, and the ether solution was dried over anhydrous $MgSO_4$ and evaporated to dryness. The residue, a viscous liquid, solidified on scratching the walls of the evaporating dish. It weighed 1.40 g (85%) and melted at 61–63 °C (lit.[17] mp 63–65 °C) after one recrystallization from hexane.

**2-Phenylisopropyl Azide.** To a solution of hydrazoic acid (ca. 0.1 mol) in 40 mL of chloroform,[16] over anhydrous $MgSO_4$, was added 1.90 g (12.5 mmol) of 2-phenylisopropyl methyl ether, followed by 2.0 mL of TFA. The resulting mixture was allowed to stand at room temperature for 24 h. Chloroform, TFA, and reaction by-products were removed in the rotary evaporator, without any heating. The residue, a pale yellow oil, weighed 1.71 g (85%). The NMR spectrum of this product showed absence of methoxy protons as well as olefinic ones; IR strong band near 2100 $cm^{-1}$ (azide).

**Reaction of 2-Phenylisopropyl Azide with Thiophenol.** 2-Phenylisopropyl azide (3.22 g, 20 mmol) was mixed with 3.0 mL of thiophenol and 5.0 mL of TFA. An exothermic reaction took place, and the mixture started foaming (gas evolution), and became cloudy. In about 10-min time two liquid phases had been separated completely. The mixture was allowed to stand at room temperature overnight. TFA was removed by evaporation under reduced pressure, benzene added, and the benzene solution was washed with sodium hydroxide solution and with water and dried over anhydrous $MgSO_4$. Evaporation of benzene left 3.45 g (76%) of 2-phenylisopropyl phenyl sulfide (NMR).

**Reaction of *tert*-Butyl Chloride with Thiophenol in the Presence of Ferric Chloride in $POCl_3$.** A mixture of *tert*-butyl chloride (12 mL, ca. 0.1 mol), thiophenol (10 mL), anhydrous ferric chloride (1.30 g, 8 mmol), and phosphorus oxychloride (50 mL) was stirred overnight at room temperature. $POCl_3$ was removed by evaporation in the rotary evaporator, the residue was taken up in 100 mL of benzene, and the benzene solution was washed successively with water, sodium hydroxide solution, and water and dried over anhydrous $MgSO_4$. Removal of benzene in the rotary left 16.35 g (98%) of *tert*-butyl phenyl sulfide (NMR). Employing glacial acetic acid as the reaction medium instead of $POCl_3$, significantly lower yields of *tert*-butyl phenyl sulfide were obtained, namely, 48 and 53% for duplicate runs.

**Benzhydryl Benzoate.** This ester was prepared in 50-mmol run by azeotropically distilling the water from a benzene solution of equimolar amounts of benzhydrol and benzoic acid, containing 1 drop of concentrated sulfuric acid. The end of the reaction can be noticed from the appearance of a yellow-orange coloration, yield 65%, mp 90–92 °C from hexane (lit.[18] mp 88–89 °C).

**Acknowledgment.** We thank Miss M. Avgerinou and Mrs. M. Voyadji for laboratory assistance.

**Registry No.**—Thiophenol, 108-98-5; phenol, 108-95-2; *sec*-butyl bromide, 78-76-2; hydrazoic acid, 7782-79-8; *tert*-butyl chloride, 507-20-0; *tert*-butyl phenyl sulfide, 2396-68-1; benzhydryl benzoate, 7515-28-8; 2-phenylisopropyl azide, 32366-26-0; benzoic acid, 65-85-0.

## References and Notes

(1) This is not a typical nucleophilic displacement. The attacking species is thiophenol rather than thiophenoxide ion.
(2) See, for example, K. B. Wiberg, "Physical Organic Chemistry", Wiley, New York, N.Y., 1966, p 421.
(3) S. Winstein, E. Grundwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951).
(4) C. D. Ritchie, *Acc. Chem. Res.*, **5**, 348 (1972), and references cited therein.
(5) E. E. Reid, "Organic Chemistry of Bivalent Sulfur", Vol. II, Chemical Publishing Co., New York, N.Y., 1960, p 17, and references cited therein.
(6) An idea about the difference in basicity between $PhCH_2OCH_3$ and $PhCH_2OCH_2CH_3$ could be taken from the gas-phase proton affinities of $Me_2O$ and $Et_2O$, 187 and 199 kcal/mol, respectively.[7]
(7) M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, **73**, 4328 (1969); J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).
(8) D. Bethell and V. Gold, "Carbonium Ions an Introduction", Academic Press, New York, N.Y., 1967, p 65.
(9) Based on comparison of the effect of *o*- and *p*-chloro substituents on the ionization of trityl chlorides in the presence of $HgCl_2$.[10]
(10) J. W. Bayles, A. G. Evans, and J. R. Jones, *J. Chem. Soc.*, 1020 (1957).
(11) Ferric chloride in $POCl_3$ appears to be a better ionizing medium than ferric chloride in glacial acetic acid.[12] In the latter system *t*-BuCl gave significantly lower yields of *t*-BuSPh. See Experimental Section.

(12) J. L. Cotter and A. G. Evans, *J. Chem. Soc.*, 2988 (1959).
(13) See, for example, M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957).
(14) S. Sugasawa and K. Fujiwara, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 72.
(15) M. Schlosser, *Newer Methods Prep. Org. Chem.*, **5**, 301 (1968).
(16) H. Wolff, *Org. React.*, **3**, 327 (1946).
(17) Yu. A. Bruk and F. Yu. Rachinskii, *Zh. Org. Khim.*, **3**, 2174 (1967).
(18) L. Horner and H. Fernekess, *Chem. Ber.*, **94**, 712 (1961).

## Salicylidene–Thiolactone Rearrangement. A Direct Synthesis of 4*H*-2-Arylthieno[3,2-*c*][1]benzopyran-4-ones

Ned D. Heindel,* John A. Minatelli, and Diane Harris

*Department of Chemistry, Lehigh University, Bethiehem, Pennsylvania 18015*

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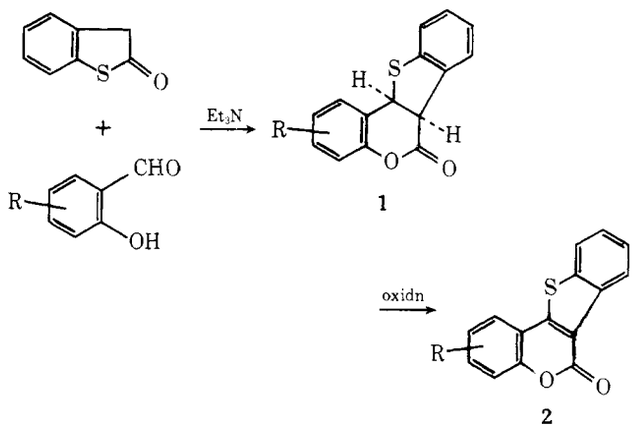
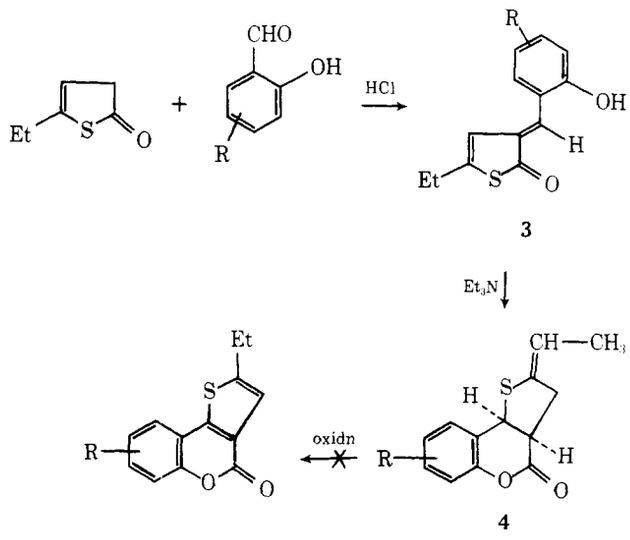
Previous publications from these laboratories have reported two related molecular transformations: the benzylidene–thiolactone rearrangement[1] and the salicylidene–thiolactone rearrangement.[2,3] In one of these, condensation of salicylaldehydes with thianaphthen-2-ones led to dihydrothienobenzopyranones (1) which upon oxidation gave the fully aromatized forms (**2**)[2] (see Scheme I). The salicylidene intermediates (**3**) were actually isolated in the condensation of 5-ethyl-4-thiolen-2-one and were rearranged to dihydrothienobenzopyranones (**4**).[3] Oxidations of the latter were unsuccessful and this resistance has been attributed to the exocyclic unsaturation in **4** (see Scheme II).

Scheme I



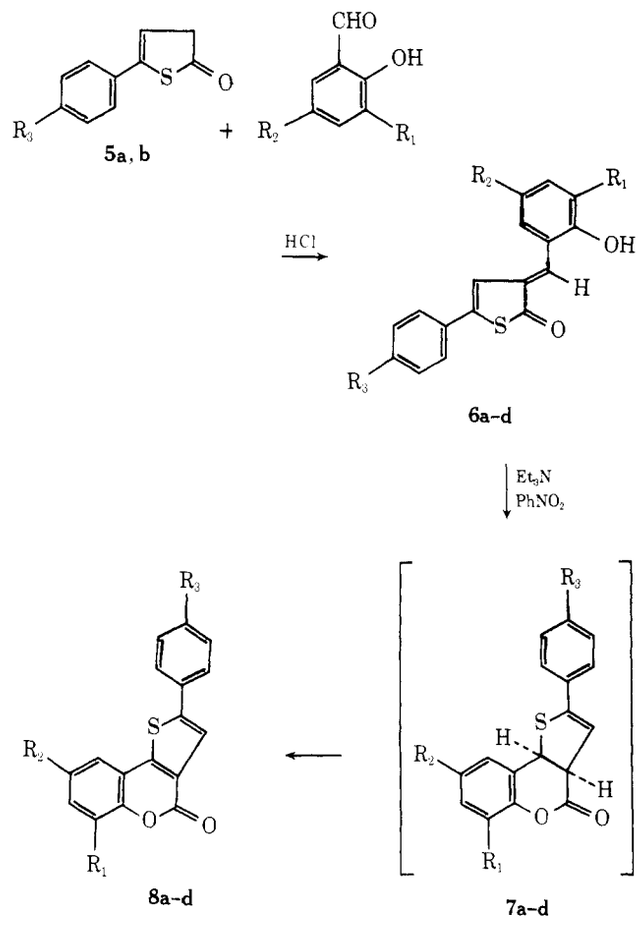
Scheme II



Several new thienobenzopyrans which bear unsaturation at the ring fusion locus have demonstrated potency as tranquilizers, analgesics, and antipyretics.[4-6] Although our earlier studies with 5-ethyl-4-thiolen-2-one did not lead to such oxidized products, we wish to report a new method which applies the salicylidene–thiolactone rearrangement to the direct preparation of such fully aromatized thienobenzopyranones. In this procedure, attachment of an aryl moiety at C-5 of the thiolenone prevents exocyclic unsaturation in the rearranged intermediate and greatly facilitates dehydrogenative oxidation.

These 5-aryl-4-thiolen-2-ones (**5a, 5b**) were prepared by sulfuration and cyclization of β-aroylpropionic acid according to a method developed by Kosak.[7] Although highly labile to oxidative formation, especially in basic media, of indigoid dimers,[7] these thiolactones could be condensed with salicylaldehydes under acidic conditions to yield stable, crystalline salicylidene derivatives (see Scheme III). These compounds (**6a–d**) were orange to red solids which gave positive $FeCl_3$ tests and which displayed carbonyl absorptions at 1653 ± 10 $cm^{-1}$. Only one vinylic hydrogen could be detected in the $^1H$ NMR spectrum and that resonance invariably fell within the aromatic complex. It thus appears that these salicylidenes possess the more sterically favored trans configuration (vinyl proton cis to carbonyl). Earlier reports have indicated a greater anisotropic deshielding for trans vinyls in closely related systems.[8-10]

Scheme III



While stable to nonbasic refluxing solvents at temperatures up to 80 °C, these salicylidenes underwent facile rearrangement—apparently after initial isomerization to a cis configuration—with amine bases at temperatures as low as 5–10 °C. Rearrangements carried out with triethylamine in chloroform, even under nitrogen atmosphere, invariably gave difficultly