The Conversion of Phenols to Thiophenols *via* Dialkylthiocarbamates[1]

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Received May 9, 1966

A number of phenols and hydroxyheterocyclic compounds have been converted to the corresponding thiol compounds by the route, phenol to O-aryl dialkylthiocarbamate to S-aryl dialkylthiocarbamate to thiophenol. Methods for accomplishing each step in high yield are described. Since the thiol compounds formed are readily desulfurized by heating with Raney nickel, a useful way of replacing aromatic hydroxyl groups by hydrogen is at hand.

The conversion of a phenol to the corresponding thiophenol represents a transformation for which there has been developed no good general method to date. Prior to the work herein reported this conversion had been effected by pyrolysis of di-O-aryl thiocarbonates (I), to O-aryl S-aryl thiocarbonates (II).[2] Further work showed that over-all conversion in the region of 20–28% of pure materials were obtained.[3] An obvious limitation of this route is that the maximum yield possible is 50% with respect to conversion of a phenol to the corresponding thiophenol.

$$\underset{\text{I}}{C_6H_5OCSOC_6H_5} \xrightarrow{\Delta} \underset{\text{II}}{C_6H_5OCOSC_6H_5}$$

We now report that pyrolysis of O-aryl dialkylthiocarbamates (III) affords S-aryl dialkylthiocarbamates (IV) in high yields.[4,5] Since phenols are readily converted into the corresponding O-aryl dialkylthiocarbamates (III) in high yield by treatment with dialkylthiocarbamyl chlorides and the S-aryl dialkylthiocarbamates (IV) are readily hydrolysed to the corresponding aryl mercaptans, a general method is now available for the conversion of phenols to thiophenols. In addition, since the hydrogenolysis of S-aryl thiocarbamates to hydrocarbons by Raney nickel proceeds in high yield (see Experimental Section), the over-all conversion of a phenol to the corresponding hydrocarbon may readily be accomplished. Some typical examples of the rearrangements are given in Table I.

$$ArOH \longrightarrow \underset{\text{III}}{ArOCSNR_2} \xrightarrow{\Delta} \underset{\text{IV}}{ArSCONR_2} \longrightarrow ArSH \longrightarrow ArH$$

The experiments summarized in Table I involved heating of the starting materials neat, except for the few cases noted in which sulfolane was used as solvent. The pyrolysis product (after 25–30 min of heating) was vacuum distilled or sublimed to yield products indicated in Table I. The purity of these materials was a minimum of 95%, as indicated by tlc or nmr analysis or both. The melting points of such products were in general very near that of the recrystallized products. In those cases where the yields are not very high, the impurity was not starting material. Rather, decomposition products, not examined in detail, were present. The purpose of this work, in general, was to explore the generality of the method rather

TABLE I

PYROLYSIS OF O-ARYL DIMETHYLTHIOCARBAMATES, $ArOCSN(CH_3)_2$, TO S-ARYL DIMETHYLTHIOCARBAMATES, $ArSCON(CH_3)_2$

Ar	Temp,[a] °C	% yield[b]
2-Nitrophenyl (**1**)	170	90
4-Nitrophenyl (**2**)	180	95–100
3-Nitrophenyl (**3**)	235	95–100
4-Pyridyl (**4**)	200	80
2-Pyridyl (**5**)	210	95
3-Pyridyl (**6**)	250	95
4-Acetophenyl (**7**)	220	95–100
4-Carboxyphenyl (**8**)	220	75[c]
2-Carbomethoxyphenyl (**9**)	220	95
4-Carbomethoxyphenyl (**10**)	220	95–100
2,4,5-Trichlorophenyl (**11**)	220	95–100
3-Trifluoromethylphenyl (**12**)	250	95–100
2,3,5,6-Tetramethylphenyl (**13**)	275	80[d]
4-*t*-Butylphenyl (**14**)	270	95–100
2-Methoxyphenyl (**15**)	280	90
4-Methoxyphenyl (**16**)	290	83
4-Hydroxyphenyl (**17**)	280	20
4-Acetamidophenyl (**18**)	280	90[c]
3-Dimethylaminophenyl (**19**)	280	95–100
4-Dimethylaminophenyl (**20**)	295	70
2-Acetophenyl (ethylene ketal) (**21**)	275	83
2-Naphthyl (**22**)	285	80[d]
3-Phenanthryl (**23**)	250	95–100
2,6-Di-*t*-butyl-4-methylphenyl (**24**)	335	13
Bishydroquinone (**25**)	270	95–100
Bisdurohydroquinone (**26**)	285	95[d]
2-Methylmercapto-4-pyrimidyl (**27**)	130	95–100
Estradiol, 17-acetate[d] (**28**)	270	40
Estrone (**29**)	270	95[c]

[a] The temperature necessary for disappearance in 20 min of the bands in the 1530–1560- (6.5–6.4 μ) and 1190–1230-cm^{-1} (8.4–8.1 μ) regions characteristic of the O-aryl dialkylthiocarbonates (III). After much of the work reported in Table I had been completed, it was discovered that samples deemed to be rearranged completely by infrared analysis above described were not completely free of starting O-aryl compounds III as shown by tlc on silica gel. In five or six representative cases, the experiments were repeated except that an additional 10 min of heating at the designated temperature was effected. The starting materials, III, were then absent. Hence it is assumed that similar results would be obtained in every case in which high yields were obtained.

[b] The per cent yield is not accurate but was estimated by isolation of essentially pure product. When thin layer chromatography of the crude pyrolysis product showed that essentially only one compound was present, the yield is reported as 95–100%. In all such cases high yields (>90%) of pure product were isolated by suitable means.

[c] Run in sulfolane, yields determined by isolation.

[d] Isolated yield. Experiments were run by Fred Hetzel.

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[1] The work herein reported was supported by a grant from the Upjohn Co., Kalamazoo, Mich.

[2] A. Schönberg and L. Vargha, *Ber.*, **63**, 178 (1930); A. Schönberg, L. Vargha, and W. Paul, *Ann.*, **483**, 107 (1930).

[3] (a) H. R. Al-Kazimi, D. S. Tarbell, and D. Plant, *J. Am. Chem. Soc.*, **77**, 2479 (1955). See this article for references to other rearrangements from oxygen to sulfur. (b) D. H. Powers and D. S. Tarbell, *ibid.*, **78**, 70 (1956).

[4] Since this work was done, the rearrangement of certain O-(2-alkyl-4,6-dinitrophenyl)dialkylthiocarbamates to the corresponding S-aryl compounds has been reported. However, the corresponding mercaptans could not be produced; see J. D. Edwards and M. Pianka, *J. Chem. Soc.*, 7338 (1965).

[5] The description of the vapor phase rearrangement at 400° of two O-aryldiethylthiocarbamates to the corresponding S-aryl compound has been reported by H. Kwart and E. R. Evans [*J. Org. Chem.*, **31**, 410 (1966)].

than to run detailed studies in any particular case in order to obtain maximum yields.

The rearrangements reported in Table I could be effected by heating at lower temperatures for longer times. For example, **10** and **11** had rearranged to greater than 90% after heating for 4.5 hr at 180°. Attempts to lower the temperature needed for rearrangement of **2** and **20** by adding small amounts of boron fluoride etherate, aluminum, zinc, and ferric chlorides did not yield encouraging results. However, catalytic amounts of boron trifluoride and hydrogen chloride lowered by 60° the temperature needed to cause rearrangement of **6** in 20 min.

The boron trifluoride and hydrogen chloride salts of the 2- and 4-pyridyl **5** and **4** rearranged at room temperature as did the acetyl 4-pyridinium chloride analog. The ready rearrangement of the salts of the 2- and 4-pyridyl compounds at room temperature indicates that this reaction should find wide application in comparable nitrogen heterocyclic systems.

The O-aryl dialkylthiocarbamates (III), were prepared by three general methods, shown below, which are described in detail in the Experimental Section.

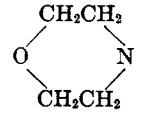
$$\text{ArONa} + \text{R}_2\text{NCSCl} \longrightarrow \text{ArOCSNR}_2 + \text{NaCl} \quad \text{(A)}$$

$$\text{ArOH} + \text{R}_2\text{NCSCl} + \text{R}_3\text{N} \longrightarrow \text{ArOCSNR}_2 + \text{R}_3\text{NHCl} \quad \text{(B)}$$

$$\text{ArOCSCl} + 2\text{R}_2\text{NH} \longrightarrow \text{ArOCSNR}_2 + \text{R}_2\text{NHCl} \quad \text{(C)}$$

Almost all of the O-aryl dialkylthiocarbamates were prepared by method A. The dimethyl compounds were preferred as they crystallized more readily and had higher melting points than the diethyl analogs.

The question as to which Z group, in compounds of formula, ArOCSZ, would be more effective in promoting rearrangement to ArSCOZ compounds received some attention. From our experience the Z groups $(CH_3)_2N$, $(C_2H_5)_2N$, and



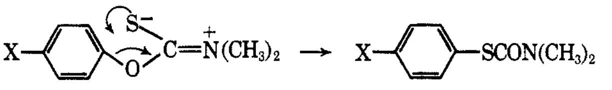
were best and roughly of equal value. For example, the pyrolysis of diethyl analogs of **11** and **25**, Table I, and of morpholino analogs of **2** and **14** gave the rearranged S-aryl compounds in comparable yields under comparable conditions. The rearrangements of O-*p*-nitrophenyl methylphenylthiocarbamate and of O-*p*-nitrophenyl methyl-*p*-nitrophenylthiocarbamate to the corresponding S-aryl compounds also proceeded well. However, if only a monosubstituted nitrogen group is present, *e.g.*, Z = RNH, pyrolysis resulted in cleavage to the isothiocyanate, RNCS, and ArOH.

The pyrolysis of O-*p*-*t*-butylphenyl thiobenzoate, *e.g.*, Z = C_6H_5, for 20 min at 285° yielded only 50% of S-*p*-*t*-butylphenyl thiobenzoate, whereas pyrolysis of **14**, Table I, underwent quantitative rearrangement at 270° in 20 min.

Aside from the fact that pyrolysis of di-O-aryl thiocarbonates (I) can give at best a 50% yield of O-aryl S-aryl thiocarbonates (II) the rearrangement of such compounds takes place considerably less readily than that of the corresponding O-aryl thiocarbamates. For example, pyrolysis of di-O-*p*-nitrophenyl thiocarbonate[3a] for 20 min at 240° afforded less than 50% of rearranged product, whereas the rearrangement of O-*p*-nitrophenyl dimethylthiocarbamate (**2**), Table I, was complete at 180° in 20 min. With the thought that the substitution of a methyl group for one *p*-nitrophenyl group in di-O-*p*-nitrophenyl thiocarbonate might improve the yield of the S-aryl compound, O-methyl O-*p*-nitrophenyl thiocarbonate was prepared and pyrolyzed at 220° for 20 min. No rearrangement to an S-aryl compound of any kind was observed as a mixture of *p*-nitroanisole and S-methyl *p*-nitrophenyl thiocarbonate was obtained.[6]

Although rearrangement of many O-aryl dimethylthiocarbamates to the corresponding S-aryl compounds was successful (see Table I) the following O-aryl analogs did not yield the S-aryl compounds: *o*-acetylphenyl, *o*-acetoxyphenyl, *o*-hydroxyphenyl, *o*-dimethylthiocarbamoylphenyl, and *p*-aminophenyl. In all of these cases, decomposition set in well below the temperature needed for rearrangement. In the case of the *o*-acetylphenyl compound conversion of the acetyl group into the corresponding ketal with ethylene glycol yielded a compound which could be rearranged smoothly (see **21**, Table I).

With regard to the effect of structure on the rate of rearrangement of O-aryl dimethylthiocarbamates, examination of the data in Table I reveals that the presence of electron-attracting groups in the aryl portion lowers the temperature needed to a considerable degree.[3b] Also, as noted above, rearrangement of the boron trifluoride and hydrogen chloride salts of **4** and **5** occurred at room temperature. These observations, together with the fact that a dialkylamino group is much better as a Z group than the phenyl or phenoxy group in promoting reaction in compounds of the type ArOCSZ, supports the suggestion[3b] that the mechanism of the rearrangement involves nucleophilic attack of the sulfur at the carbon holding the oxygen. The desired polarization is



assisted by the dialkylamino group. The fact that O-*p*-nitrophenyl dimethylthiocarbamate (**2**) rearranges more readily than O-*p*-nitrophenyl methyl-*p*-nitrophenylcarbamate (20 min at 200° needed) supports the above mechanistic interpretation.

The rearrangement of O-*p*-nitrophenyl dimethylthiocarbamate to S-*p*-nitrophenyl dimethylthiocarbamate was shown to be a first-order reaction (see Experimental Section). Presumably, all of the other similar rearrangements proceed intramolecularly.

On alkaline hydrolysis the S-aryl dimethylthiocarbamates afforded the corresponding thiols in high yield. Although all of the S-aryl thiocarbamates studied were not hydrolyzed to thiols, the high yields obtained (see Experimental Section) in selected cases show that the reaction is undoubtedly general. Thus the conversion of a phenolic compound to the thiophenolic analog *via* the O-aryl and S-aryl dialkylthiocarbamyl derivatives is an excellent one. This finding, coupled with the fact that thiohydrogenolysis of the

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[6] After completion of this experiment the pyrolysis of O-methyl O-*p*-nitrophenyl thiocarbonate at 180° for 8 hr to yield *p*-nitroanisole (75%) and S-methyl *p*-nitrophenyl thiocarbonate (25%) was reported by G. Hilgetag and R. Phillipson [*Monatsber. Deut. Akad. Wiss., Berlin*, **6**(**8**), 585 (1964); *Chem. Abstr.*, **62**, 5165*h* (1965)].

thiophenolic compounds is readily accomplished by treatment with Raney nickel[7] make possible an excellent was of replacing a phenolic hydroxyl by hydrogen (see also statement in ref 5). In the latter connection, the failure of S-2-naphthyl dimethylthiocarbamate and S-2,3,5,6-tetramethylphenyl dimethylthiocarbamate to yield more than 30% of naphthalene and durene shows that hydrolysis to thiols is necessary prior to Raney nickel treatment if high yields are to be obtained.

Experimental Section[8]

Preparation of O-Aryl Dimethylthiocarbamates.—Typical exampes are given of the three routes, A–C, mentioned in the introductory part. Route A was used most often. The physical constants and analyses of these compounds are listed in Table II.

Route A. Example I. O-3-Pyridyl Dimethylthiocarbamate (6).—To a cooled solution of 58 g (0.6 mole) of 3-pyridinol dissolved in 450 ml of dimethylformamide was added, in small portions, 17 g (0.6 mole) of sodium hydride. After hydrogen evolution ceased the solution was cooled to 10° in an ice bath and 100 g (0.8 mole) of dimethylthiocarbamoyl chloride[9] added all at once. The temperature rose rapidly to 25° and then slowly to 40°. The cooling bath was removed and the mixture heated during 1 hr to 80°. After cooling the mixture was poured into 2 l. of 1% potassium hydroxide. The resulting dark solution was saturated with sodium chloride and then extracted with two 1-l. portions of benzene–Skellysolve B (4:1) (petroleum ether bp 60–70°). Organic extracts were washed with 1-l. of water and 800 ml of 5% hydrochloric acid. The acid wash was cooled and carefully neutralized with 10% potassium hydroxide. The resulting dark red oil was extracted with 1 l. of benzene–Skellysolve B (4:1). The organic extract was washed with saturated sodium chloride, filtered through anhydrous magnesium sulfate, and concentrated to dryness to yield 98 g of a dark oil. Vacuum distillation yielded 95 g (90%) of **6** as a light yellow liquid, bp 125–130° at 0.4 mm.

Example II. O-*p*-*t*-Butylphenyl Dimethylthiocarbamate (14).—To a solution of 21 g (0.17 mole) of dimethylthiocarbamoyl chloride[9] in 140 ml of dimethylformamide at 14° in an ice–water bath was added, all at once, 17.6 g (0.10 mole) of dry sodium *p*-*t*-butylphenolate. The temperature rose rapidly to 26° and leveled. The cooling bath was removed and the reaction was stirred 1.5 hr at 30–34°. The mixture was added to 300 ml of water and extracted twice with 300-ml portions of benzene–Skellysolve B (4:1). The organic extracts were washed with water, 5% potassium hydroxide, and saturated sodium chloride and filtered through anhydrous magnesium sulfate. Upon concentrating to dryness 22.6 g of yellow solid was obtained which yielded, after recrystallization from 100 ml of methanol, 21.4 g (90.5%) of white crystalline **14**, mp 97–99°.

In a similar way, treatment of hydroquinone with diethylthiocarbamyl chloride[10] yielded O,O-bis-*p*-phenylene diethylthiocarbamate, mp 156–160°, in 40% yield.

Anal. Calcd for $C_{16}H_{24}N_2O_2S_2$: C, 56.4; H, 7.1. Found: 56.4; H, 7.4.

Treatment of catechol with dimethylthiocarbamyl chloride yielded O,O-bis-*o*-phenylene dimethylthiocarbamate, mp 112–113°, in 25% yield. On pyrolysis at 260° black tar was formed.

Anal. Calcd for $C_{12}H_{16}N_2O_2S_2$: C, 50.7; H, 5.7. Found: C, 50.8; H, 5.6.

In addition to the above bis compound a quantity of O-*o*-hydroxyphenyl dimethylthiocarbamate was obtained by extraction with base. All attempts to obtain an analytically pure sample failed. Pyrolysis of reasonable pure materials yielded black tar. Accordingly the crude product was treated with acetyl chloride in chloroform to yield a small amount of O-*o*-acetoxyphenyl dimethylthiocarbamate, mp 102–104°. Pyrolysis of this also produced black tar.

Anal. Calcd for $C_{11}H_{13}NO_3S$: C, 55.2; H, 5.5. Found: C, 55.4; H, 5.7.

Processing of *p*-aminophenol by route A afforded O-*p*-aminophenyl dimethylthiocarbamate, mp 115–118°, in 30% yield.

Anal. Calcd for $C_9H_{12}N_2OS$: C, 55.1; H, 6.2. Found: C, 55.3; H, 6.5.

Route B.—Procedure B, less often used, involved the reaction of a phenol with a disubstituted thiocarbamoyl chloride in dimethylformamide containing a tertiary amine. This procedure worked well with phenols bearing electron-withdrawing substituents. With phenols bearing electron-donating substituents poor yield were obtained. The procedure worked well with strong bases such as 1,4-diazabicyclo[2.2.2]octane (Dabco)[11] or N-methylmorpholine. With triethylamine or pyridine very poor yields were obtained. The following examples illustrate this procedure.

Example I. O-*p*-Nitrophenyl Dimethylthiocarbamate (2).—To 13.9 g (0.1 mole) of *p*-nitrophenol dissolved in 150 ml of dimethylformamide was added 22.4 g (0.2 mole) of Dabco[11] and 18.5 g (0.15 mole) of dimethylthiocarbamoyl chloride. The resulting cloudy solution was stirred for 0.5 hr at 30–35° and then heated over a 0.5 hr period to 75°. After cooling 300 ml of water was added and the mixture was filtered. The solid was washed with 300 ml of water and dried at 50° to yield 24 g of crude yellow product which yielded, after three recrystallizations from ethanol–benzene (4:1), 20.8 g (92%) of yellow crystalline **2**, mp 150–153°.

Example II. O-2-Carbomethoxyphenyl Dimethylthiocarbamate (9).—To a solution of 7.6 g of methyl salicylate in 75 ml of dimethylformamide containing 16.8 g of Dabco was added 18.5 g of dimethylthiocarbamyl chloride in one portion. The temperature rose rapidly to 50°. The mixture was held at 50° for 5 hr and was then poured into 300 ml of water. The product was taken into benzene–hexane and washed with dilute hydrochloric acid and sodium hydroxide. After drying over magnesium sulfate the solvents were removed and the residue was crystallized twice from methanol to yield 9.6 g (80%) of colorless **9**, mp 96–98°. The analytical sample melted at 98–100°.

Route C.—The required O-aryl chlorothioformates were prepared essentially as described[12] and used without analysis.

Example I. O-*p*-*t*-Butylphenyl Morpholinothiocarbamate.—To a solution of 8.0 g of O-*p*-*t*-butylphenyl chlorothioformate in 150 ml of dry ether was added a solution of 10 ml of N-methylmorpholine and 8 ml of morpholine. After 30 min the mixture was washed successively with 5% HCl, 5% Na_2CO_3, and saturated NaCl solution, and filtered through anhydrous $MgSO_4$. The ether was distilled and the residue was recrystallized twice from methanol to yield 7.5 g (76%) of product, mp 135–137°.

Anal. Calcd for $C_{15}H_{21}NO_2S$: C, 64.5; H, 7.6. Found: C, 64.2; H, 7.7.

Similarly, this chlorothioformate was treated with aniline to produce O-*p*-*t*-butylphenyl phenylthiocarbamate, mp 142–144°, in 45% yield.

Anal. Calcd for $C_{17}H_{19}NOS$: C, 71.5; H, 6.7. Found: C, 71.6; H, 6.8.

Example II. O-*p*-Nitrophenyl Methylphenylthiocarbamate.—To a solution of 6.6 g of O-*p*-nitrophenyl chlorothioformate,[12] mp 58–60°, in 100 ml of benzene was added 8.5 g of N-methylaniline. After 15 min the solid was removed by filtration and the filtrate was washed successively with 5% HCl, 5% Na_2CO_3, and saturated NaCl solution, and filtered through $MgSO_4$. Removal of the solvent left an oil which solidified. Two recrystallizations from 200-ml portions of ethanol yielded 6.8 g (77%) of product, mp 130–132°.

Anal. Calcd for $C_{14}H_{12}N_2O_3S$: C, 58.3; H, 4.2. Found: C, 58.6; H, 4.3.

Similarly, O-*p*-nitrophenyl methyl-*p*-nitrophenylthiocarbamate, mp 196–203°, and O-*p*-nitrophenyl morpholinothiocarbamate, mp 186–191°, were prepared by treatment of the above chlorothioformate with methyl-*p*-nitrophenylaniline and morpholine, respectively.

Anal. Calcd for $C_{14}H_{11}N_3O_5S$: C, 50.4; H, 3.3. Found: C, 50.3; H, 3.5.

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(7) M. L. Wolfrom and J. V. Karabinos, *J. Am. Chem. Soc.*, **66**, 909 (1944).

(8) All melting points are uncorrected but were taken with standardized thermometers. All microanalyses through the courtesy of the Upjohn Co., Kalamazoo, Mich.

(9) Prepared as described in "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 310, from bis(dimethylthiocarbamoyl)disulfide, "Thiram." We acknowledge with thanks generous gifts of Thiram from the Pennsalt Manufacturing Co., Three Penn Center, Philadelphia, Pa.

(10) We thank the Pennsalt Manufacturing Co., for a generous gift of this reagent.

(11) We thank the Houdry Process Co., Marcus Hook, Pa., for generous samples of Dabco.

(12) A. F. McKay, D. L. Garmaise, G. Y. Paris, S. Gelblum, and R. V. Ranz, *Can. J. Chem.*, **38**, 2042 (1960).

TABLE II

O-ARYL AND S-ARYL DIMETHYLTHIOCARBAMATES[a]

Compd	Mp, °C (mm)	Route[b]	Formula	Calcd, %		Found,[c] %	
				C	H	C	H
1	112–113	A	$C_9H_{10}N_2O_3S$	47.8	4.6	47.8	4.7
1a	30–32		Same			47.7	4.6
2	150–153	B	Same			48.1	4.7
2a	122–124		Same			47.7	4.5
3	153–155	B	Same			47.9	4.6
3a	117–120		Same			48.1	4.8
4	82–83	A[d]	$C_8H_{10}N_2OS$	52.7	5.5	52.4	5.6
4a	69–71		Same			52.8	5.8
5	74–77	A	Same			52.8	5.7
5a	130–135[e] (0.2)		Same			52.9	5.7
6	125–130[e] (0.4)		Same			52.4	5.7
6a	125–130[f] (0.8)		Same			52.9	5.7
7	99–103	A	$C_{11}H_{13}NO_2S$	59.2	5.9	59.4	6.0
7a	106–109		Same			59.5	5.6
8	231–245[g]	*h*	$C_{10}H_{11}NO_3S$	53.3	4.9	53.3	5.2
8a	192–195		Same			53.6	5.2
9	98–100	A	$C_{11}H_{13}NO_3S$	55.2	5.5	55.4	5.5
9a	156–164[i]		Same			55.1	5.5
10	100–102	A	Same			55.4	5.6[j]
10a	91–93[k]		Same			55.0	5.5
11	139–142	A	$C_9H_8Cl_3NOS$	38.0	2.8	38.0	2.9
11a	153–155		Same			38.1	2.8
12	64–65	A	$C_{10}H_{10}F_3NOS$	48.2	4.0	48.5	4.3
12a	100–103[l]		Same			48.2	4.2
13	118–119[m]	A	$C_{13}H_{19}NOS$	65.8	8.0	65.8	8.2[n]
13a	92–93		Same			65.9	8.2[o]
14	97.5–99	A	Same			66.1	8.1
14a	70–71.5		Same			66.0	8.2
15	61–62	A	$C_{10}H_{13}NO_2S$	56.8	6.2	57.1	6.5
15a	93–95		Same			57.0	6.3
16	82–84		Same			57.0	6.3
16a	94–96		Same			56.7	6.2
17	123–126	A	$C_9H_{11}NO_2S$	54.8	5.6	54.9	5.4
17a	183–194		Same			54.9	5.4
18	185.5–187.5	A	$C_{11}H_{14}N_2O_2S$	55.5	5.9	55.2	5.9
18a	143–145		Same			55.6	5.9
19	82–84	A	$C_{11}H_{16}N_2OS$	58.9	7.2	59.0	7.2
19a	155–160[p]		Same			58.9	7.1
20	104–106	A	Same			59.2	7.1
20a	126–130		Same			59.2	7.0
21	78–80	*q*	$C_{13}H_{17}NO_3S$	58.4	6.4	58.5	6.5
21a	150–155[r]		Same			58.4	6.4
22	92–93[m]	A	$C_{13}H_{13}NOS$	67.6	5.6	67.3	5.8[s]
22a	113–114[m]		Same			67.5	5.8[t]
23	107–108	A	$C_{17}H_{15}NOS$	72.5	5.4	72.7	5.4
23a	92–95		Same			72.8	5.5
24	120–121	A	$C_{18}H_{29}NOS$	70.3	9.5	70.1	9.8
24a	181–186[t]		Same			70.5	9.3
25	214–216	A	$C_{12}H_{16}N_2O_2S_2$	50.7	5.7	50.8	5.6
25a	200–202		Same			50.5	5.7
26	235–236	A	$C_{16}H_{24}N_2O_2S_2$	56.5	7.1	56.5	7.1[u]
26a	247–248		Same			56.5	7.1[v]
27	80–81	A	$C_8H_{11}N_3OS_2$	41.9	4.8	42.1	5.1
27a	66–68		Same			42.0	5.0
28	182–185	A	$C_{23}H_{31}NO_3S$	68.8	7.8	68.8	7.6
28a	178–181		Same			69.0	7.8
29	215–219	A	$C_{21}H_{27}NO_2S$	70.5	7.6	70.5	7.9
29a	180–184		Same			70.2	7.7

[a] The compounds are listed according to the numbering system used in Table I. All O-aryl compounds have the same number and all rearranged S-aryl compounds have the same number with the suffix a. [b] The capital letters A–C refer to the three methods of preparation described in the discussion. [c] All analyses by the Upjohn Co. analytical department. [d] The silver salt was used instead of the sodium salt. [e] Liquid, boiling point pressure in parentheses. [f] H. M. Wuest and E. H. Sakal, *J. Am. Chem. Soc.*, **73**, 1210 (1951). [g] Higher melting O-aryl compounds melted with decomposition. Melting ranges affected by rate of heating. [h] Prepared by acid hydrolysis of **10**. [i] Boiling point at 0.5 mm. [j] *Anal.* Calcd for $C_{11}H_{13}NO_3S$: N, 5.9; S, 13.4. Found: N, 5.7; S, 13.4. [k] Boiling point 170–175° at 0.6 mm. [l] Boiling point at 0.2 mm. [m] Prepared by Fred Hetzel. [n] *Anal.* Calcd: N, 5.9. Found: N, 6.0.[w] [o] *Anal.* Calcd: S, 13.5; N, 5.9. Found: S, 13.7; N, 6.0.[w] [p] Boiling point 155–160° at 0.2 mm. [q] Prepared from O-*o*-acetylphenyl dimethylthiocarbamate by ketalization. [r] Boiling point at 0.3 mm. [s] *Anal.* Calcd: N, 6.1. Found: N, 6.3.[w] [t] *Anal.* Calcd: N, 6.1.[w] [u] *Anal.* Calcd: N, 8.2. Found: N, 8.3.[w] [v] *Anal.* Calcd: N, 8.2; S, 18.8. Found: N, 8.2; S, 18.9.[w] [w] Analyses in footnotes *n*, *o*, and *s*–*v* were by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Anal. Calcd for $C_{11}H_{12}N_2O_4S$: C, 49.2; H, 4.5. Found: C, 49.4; H, 4.8.

Preparation of Other Sulfur-Containing Derivatives.—By heating the sodium salt of the required phenol in dimethylformamide with thiobenzoyl chloride,[13] O-*p*-nitrophenyl thiobenzoate, mp 98–100°, and O-*p*-*t*-butylphenyl thiobenzoate, mp 80–82°, were prepared.

Anal. Calcd for $C_{13}H_9NO_3S$: C, 60.2; H, 3.5. Found: C, 60.0; H, 3.6.

Anal. Calcd for $C_{17}H_{18}OS$: C, 75.5; H, 6.7. Found: C, 75.5; H, 6.8.

O-*p*-Carboxyphenyl dimethylthiocarbamate (**8**) was prepared from O-*p*-carbomethoxyphenyl dimethylthiocarbamate (**10**) by stirring a solution containing 15 g of **10** in 60 ml of methanol and 120 ml of 10% HCl for 16 hr at reflux. The solid which precipitated on cooling was collected and washed with 400 ml of saturated $KHCO_3$ solution. Acidification of the filtrate yielded 6 g of solid which on sublimation at 150° at 0.1 mm yielded 3 g of colorless **8**, mp 231–245° dec.

Ethylene Ketal of O-*o*-Acetylphenyl Dimethylthiocarbamate (**22**).—O-*o*-Acetylphenyl dimethylthiocarbamate, mp 68–70°, was prepared from *o*-acetylphenol by method A in 60% yield.

Anal. Calcd for $C_{11}H_{13}NO_2S$: C, 59.2; H, 5.9. Found: C, 59.4; H, 5.8.

A solution of 95 g of O-*o*-acetophenyl dimethylthiocarbamate, 80 ml of ethylene glycol, and 3 drops of concentrated sulfuric acid in 400 ml of benzene was distilled into a short column topped by a phase-separating head for 24 hr. The neutral portion of the reaction products was crystallized three times from methanol to yield 60 g (53%) of colorless **22**, mp 78–80°.

Pyrolysis Experiments.—In order to arrive at the conditions for carrying out the experiments listed in Table I small amounts of the starting O-aryl dimethylthiocarbamates were heated at various temperatures for varying times. In most cases the progress of the reactions could be followed by thin layer chromatography on silica gel with development by methylene chloride–methanol mixtures or methylene chloride alone. The rearrangements could also be followed by taking infrared spectra (see footnote *a*, Table I) and by nmr measurements as the N-methyl groups of the O-aryl compounds had a doublet in the τ 7.3–7.5 [$(CH_3)_4Si$ standard] region while the S-aryl compounds had sharp singlets at τ 7.0–7.1. The S-aryl compounds prepared are listed in Table II.

The following S-*p*-nitrophenyl thiocarbamates not listed in Table II were prepared by heating of the corresponding O-*p*-nitrophenyl thiocarbamates for about 25 min at the temperature indicated: S-*p*-nitrophenyl methylphenylthiocarbamate, mp 163–165°, 180°, 100% yield; S-*p*-nitrophenyl methyl-*p*-nitrophenylthiocarbamate, mp 164–165°, 200°, 90% yield; S-*p*-*t*-butylphenyl morpholinothiocarbamate, mp 92–96°, 280°, 90% yield.

Anal. Calcd for $C_{14}H_{12}N_2O_3S$: C, 58.3; H, 4.2. Found: C, 58.5; H, 3.9. Calcd for $C_{14}H_{11}N_3O_5S$: C, 50.4; H, 3.3. Found: C, 50.5; H, 3.4. Calcd for $C_{11}H_{12}N_2O_4S$: C, 49.2; H, 4.5. Found: C, 49.3; H, 4.7. Calcd for $C_{15}H_{21}NO_2S$: C, 64.5; H, 7.6. Found: C, 64.5; H, 7.7.

After heating O,O-bis-*p*-phenylene diethylthiocarbamate at 270° for 25 min, a quantitative yield of S,S-bis-*p*-phenylene diethylthiocarbamate, mp 172–175°, was obtained.

Anal. Calcd for $C_{16}H_{24}N_2O_2S_2$: C, 56.4; H, 7.1. Found: C, 56.7; H, 7.2.

To test the effect of solvent on the rate of rearrangement, solutions of 0.5 g of **2** in 25 ml of dimethylformamide and 25 ml of 1-dodecene were heated at 155–157° for 1 hr. Similarly 0.5 g of **2** alone was heated. The material isolated from the DMF run gave a strong peak at 6.0 μ (*i.e.*, S-aryl compound) as did the neat sample. The material from the 1-dodecene run showed a very weak carbonyl absorption at 6.0 μ.

In general no need for solvent in the pyrolyses is present. However, if intermolecular reaction can occur, as in the cases of **8**, **17**, and **18**, Table I, the use of a solvent, *e.g.*, sulfolane, is recommended. When no solvent was used in these cases, the yields of products were much lower.

In order to test the molecularity of the rearrangement reaction solutions containing 50.4 and 250 mg of **2** in 5 ml of polyethylene glycol (Carbowax 400) were heated at 180° for 15 min. Ultraviolet spectral analysis,[14] using a Bausch and Lomb Spectronic 505 instrument, showed that rearrangement to **2a** had occurred to the same (within 10%) extent in the two cases. The absorption at 268 mμ (ϵ *ca.* 30,000) was used to estimate the amount of **2** present and at 320 mμ (ϵ *ca.* 10,000) to estimate **2a**.

Preparation of Thiophenols.—In principle, all of the S-aryl compounds listed in Table II could be converted into the corresponding thiophenols. Actually, only a few were so converted. In general a solution of the S-aryl dimethylthiocarbamate in methanol containing excess 10% aqueous sodium hydroxide was heated under nitrogen for times sufficient to effect hydrolysis. Isolation by appropriate procedures yielded *p*-*t*-butylbenzenethiol,[15] bp 102–105° at 7–8 mm, in 85% yield, *o*-mercaptobenzoic acid,[16] mp 160–163°, in 92% yield, 2-methylmercapto-4-mercaptopyrimidine,[17] mp 199–201°, in 81% yield, and 3-phenanthrenethiol, mp 110–112°, in 83% yield.

Anal. Calcd for $C_{14}H_{10}S$: C, 80.0; H, 4.8; S, 15.2. Found: C, 79.9; H, 4.8; S, 14.9.

In a similar way, alkaline hydrolysis of **21a** yielded an oil, bp 90–100° at 0.2–0.3 mm, in 78% yield. This oil was mainly *o*-(2-methyl-1,3-dioxolan-2-yl)benzenethiol. On low temperature crystallization from methanol the pure compound, mp 42–43°, was obtained.

Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.2; H, 6.1. Found: C, 61.5; H, 6.4.

Thiohydrogenolysis Procedure.—A solution of 12.5 g of S-2-naphthyl dimethylthiocarbamate (**22a**) and 4 g of sodium hydroxide in 50 ml of methanol was refluxed overnight under nitrogen. After acidification, 7.9 g of 2-naphthalenethiol,[18] mp 77–78°, was isolated by benzene extraction. This product in 100 ml of ethanol at reflux was treated with 40 g of Raney nickel (W-2)[19] for 8 hr. After removal of the solvent on a rotary evaporator sublimation afforded 6.2 g (98% over-all) of naphthalene, mp 78–79°. In a similar run starting with **22a**, only a 30% yield of naphthalene was obtained.

In order to test the effect of steric hindrance on the thiohydrogenolysis, 8.5 g of **13a** was hydrolyzed to durenethiol,[20] mp 60.0–61.5° in 88% yield. Hydrogenolysis of 3.5 g of this thiol as above yielded 70% of durene, mp 79–80°. One can conclude from this one experiment[14] that thiohydrogenolysis of a hindered thiol proceeds in good yield but less readily than in nonhindered cases.

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[13] E. J. Hedgley and R. C. Fletcher, *J. Org. Chem.*, **30**, 1282 (1965).

[14] We thank Mr. F. Hetzel for performing this experiment.

[15] E. Bartkus, O. Hotelling, and M. Newworth, *J. Org. Chem.*, **25**, 232 (1960).

[16] C. Wang and S. Cohen, *J. Am. Chem. Soc.*, **81**, 3005 (1959).

[17] W. Schneider and I. Halverstadt, *ibid.*, **70**, 2626 (1948).

[18] T. Lesniak [*Roczniki Chem.*, **38**, 1923 (1964)] reports mp 81°.

[19] R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 181.

[20] G. Illuminati [*J. Am. Chem. Soc.*, **80**, 4945 (1958)] reports mp 63.5–65.0°.