J. Mex. Chem. Soc. **2005,** *49(2),* 159-165.

J. Braz. Chem. Soc., Vol. 16, No. 3A, 397-403, 2005.

0103 - 5053

Article

Synthesis of 2,4-Disubstituted Thiophenols and Solid State Structures of Thiocarbamate Precursors

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Uma série de tiofenóis com diferentes *orto*-substituintes, 2,4-dimetiltiofenol, 2-*terc*-butil-4-metiltiofenol e 2-(1-adamantil)-4-metiltiofenol, os quais mostram diferentes graus de impedimento estérico na posição 2, foram preparados a partir dos correspondentes fenóis. Uma despronotação inicial dos fenóis foi obtida com o uso de NaH em dimetoxietano, seguido de tratamento com cloreto de *N*,*N*-dimetiltiocarbomoila, obtendo-se os *O*-ariltiocarbamatos. A termólise destes compostos resultou num rearranjo, obtendo-se os *S*-ariltiocarbamatos. Finalmente, a redução dos *S*-ariltiocarbamatos com $LiAlH_4$ em THF, seguido de acidificação, levou ao isolamento dos tiofenóis. Todos os produtos foram caracterizados por técnicas espectroscópicas, e para alguns tiocarbamatos a estrutura sólida foi determinada por difração de raio X.

A series of thiophenols with different *ortho*-substituents, 2,4-dimethylthiophenol, 2-*tert*-butyl-4-methylthiophenol, and 2-(1-adamantyl)-4-methylthiophenol, which display varying degrees of steric hindrance on the 2-position, was prepared from the corresponding phenols. Initial deprotonation of the phenols was achieved with NaH in dimethoxyethane, followed by treatment with *N*,*N*-dimethylthiocarbamoyl chloride, to obtain the *O*-arylthiocarbamates. Thermolysis of the latter compounds resulted in rearrangement, which yields the desired *S*-arylthiocarbamates. Finally, reduction of the *S*-arylthiocarbamates with $LiAlH_4$ in THF, followed by acidic workup, allowed the isolation of the thiophenols. All products were characterized by spectroscopic techniques, and in the case of some of the thiocarbamates the solid state structures were determined by single-crystal X-ray diffraction.

Keywords: thiols, thiophenols, thiocarbamates, bulky thiols, X-ray structure

Introduction

Thiols represent an important class of compounds due to their relevance in organic, inorganic, and materials chemistry.[1-3] Within the context of inorganic chemistry, thiols have a crucial role as thiolate ligands in coordination compounds that are relevant in both chemical and biological systems.[2,4] While in many of these systems it is desirable to have bridging thiolate ligands for building multimetallic assemblies,[5] in other cases sterically demanding thiols are necessary for the preparation of monometallic complexes.[6] This latter situation requires thiols that can create a protective pocket around the metal center in order to avoid the formation of high nuclearity species.

The most common method of preparation of thiophenols that are not commercially available involves the lithiation of aromatic halides under an inert atmosphere. Subsequent reaction of the organolithium compounds with elemental sulfur produces the corresponding thiols upon hydrolysis.[1] This method is limited by the availability of halogenated aromatic compounds required for the lithium-halogen exchange reaction, with the more widely available phenols as an alternative starting material for the synthesis of thiophenols.

Newman and Karnes developed a method for the transformation of phenols into thiophenols,[7] which involves the thermal rearrangement of *O*-arylthiocarbamates into *S*-arylthiocarbamates (Scheme 1). Thus, this methodology requires the synthesis, isolation, and characterization of both *O*- and *S*-arylthiocarbamates. Given the large number of *ortho*- substituted phenols that are commercially available, we decided to undertake the preparation of the corresponding thiophenols. The phenols considered in this work include 2,4-dimethylphenol (**1**), 2-*tert*-butyl-4-methylphenol (**2**), and 2-(1-adamantyl)-4-

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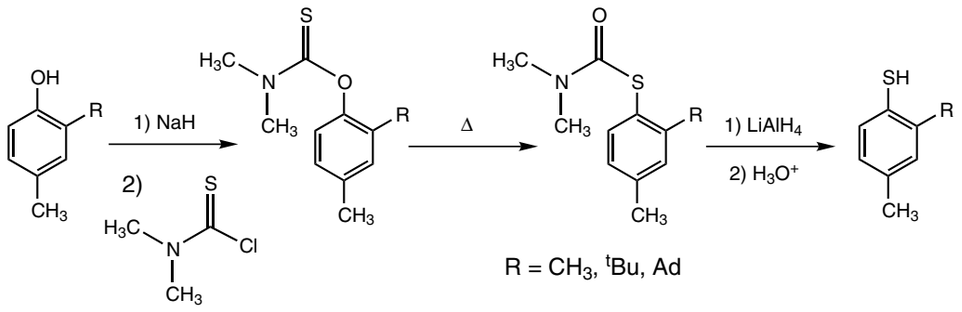


Scheme 1. Synthesis of 2,4-disubstituted thiophenols.

methylphenol (**3**), which can be compared in terms of their reactivity based on the varying degrees of steric hindrance provided by the substituent adjacent to the hydroxy or thiol groups.

Results and Discussion

Synthesis of O-arylthiocarbamates

2-alkyl-4-methylphenyl-*N*,*N*-dimethyl-*O*-thiocarbamates (alkyl = methyl, *tert*-butyl, and 1-adamantyl) were prepared from the corresponding phenols by adapting the previously described procedure.[7] The phenol with the sterically encumbering 1-adamantyl group required the longest times for the reaction to proceed to completion.

The products were characterized by standard spectroscopic techniques: Nuclear Magnetic Resonance (^{1}H and ^{13}C NMR), infrared (IR), and electron-ionization mass spectrometry (EI-MS), as well as melting point determinations and combustion analysis. The main feature in the ^{1}H NMR spectra is the presence of two sharp singlets in a 1:1 ratio, which correspond to the *N*-methyl groups of the thiocarbamoyl moiety. The non-equivalency of the nitrogen-bound methyl groups has been previously reported for related compounds.[8] In this series the presence of non-equivalent *N*-methyl groups was observed even for 2,4-dimethylphenyl-*N*,*N*-dimethyl-*O*-thiocarbamate (**4**), which features the smallest substituent in the 2-position. It is therefore reasonable to assume that, in solution, the restriction in the rotation about the C(sp^2)-N bond is electronic in nature. The two *N*-methyl resonances appear at δ 3.34 and 3.45 ppm, with those for 2-*tert*-butyl-4-methylphenyl-*N*,*N*-dimethyl-*O*-thiocarbamate (**5**) at δ 3.39 and 3.49 ppm, and those for 2-(1-adamantyl)-4-methylphenyl-*N*,*N*-dimethyl-*O*-thiocarbamate (**6**) at δ 3.42 and 3.51.

IR spectra exhibit a band for the C=S stretching at 1536, 1526, and 1553 cm^{-1} for compounds **4**, **5**, and **6**. This spectroscopic technique is useful for identifying the presence of the C=S *versus* the C=O group of the corresponding *S*-arylthiocarbamates, since the disappearance of the aforementioned bands is followed by the appearance of new stretching bands at higher frequencies, which correspond to the C=O group.

Synthesis of S-arylthiocarbamates

Thermal rearrangement of the *O*-arylthiocarbamates **4**, **5**, and **6** to 2,4-dimethylphenyl-*N*,*N*-dimethyl-*S*-thiocarbamate (**7**), 2-*tert*-butyl-4-methylphenyl-*N*,*N*-dimethyl-*S*-thiocarbamate (**8**), and 2-(1-adamantyl)-4-methylphenyl-*N*,*N*-dimethyl-*S*-thiocarbamate (**9**), respectively, was carried out neat under reduced pressure in closed systems in order to avoid loss of starting materials by sublimation at 250, 280, and 310 °C. It is evident that as the steric bulk of the *ortho*-substituent increases, the reaction temperature required for the rearrangement to occur also increases.

The *S*-arylthiocarbamates were characterized by spectroscopic techniques, melting point determination, and combustion analysis. The identity of the compounds was confirmed by EI-MS, which shows the presence of the expected molecular ions. In contrast with the spectra of the *O*-arylthiocarbamates, in the ^{1}H NMR spectrum of compound **7** a pair of broad resonances that arise from the *N*-methyl groups was observed at δ 3.02 and 3.11. For compounds **8** and **9**, the two peaks coalesce at room temperature into a single broad resonance at δ 3.08 and 3.02. As mentioned above, IR spectra clearly revealed the rearrangement of the O and S atoms. This was evidenced by the disappearance of the C=S stretching bands, and the appearance of new intense bands in the ν(C=O) region at 1654, 1653, and 1655 cm^{-1} for **7**, **8**, and **9**.

Synthesis of thiophenols

Reduction of the *S*-arylthiocarbamates with excess $LiAlH_4$ in anhydrous THF, followed by acidic workup yielded 2,4-dimethylbenzenethiol (**10**) 2-*tert*-butyl-4-

methylbenzenethiol (**11**), and 2-(1-adamantyl)-4-methylbenzenethiol (**12**). The thiols were obtained as yellow or colorless liquids upon evaporation of the organic solvents. Compound **10** was only prepared by this method to prove the feasibility of the reaction since it is a commercially available substance. An alternative synthetic procedure for **10** has been reported which minimizes the formation of the corresponding disulfide, although it requires the sulfonyl chloride as a starting material.[9]

In the ^{1}H NMR spectra of the fully characterized thiols **11** and **12**, the characteristic resonance of the thiol group was observed at δ 3.52 and 3.57. Likewise, the most prominent feature of the IR spectrum of **11** was the stretching band of the S-H group at 2567 cm^{-1}. In the case of **12**, although the corresponding S-H band appeared at 2564 cm^{-1} with low intensity, both the ^{1}H NMR and the mass spectrometry data confirm its identity. Thus, the expected molecular ions in the mass spectra of the two thiols were observed, as well as the ions of the corresponding disulfides [ArSSAr]$^+$, which are probably formed in the ionization chamber.

*Solid state structures of **4**, **5**, and **8***

Despite 2,4-dimethylbenzenethiol being a commercially available compound, there are no reports on the synthesis and properties of the *O*- and *S*-arylthiocarbamates. Therefore, the solid state structure of the *O*-arylthiocarbamate **4** was determined by X-ray crystallography. Crystal and structure refinement data are presented in Table 1. Monoclinic crystals of **4** (space group $P2_1/c$) were obtained by slow evaporation of a concentrated CH_2Cl_2 solution. In the solid state structure of **4**, the thiocarbamoyl π-system appears to be delocalized onto both N and O atoms, as evidenced by the coplanarity of O1, C9, S1, N1, C10 and C11. This is also reflected in the bond angles around N1 [C9-N1-C10 123.3(2)°, C9-N1-C11 120.8(2)°, C10-N1-C11 115.8(2)°], and O1 [C1-O1-C9 121.0(2)°], which correspond to sp^2-hybridized atoms. The planarity of the thiocarbamoyl group forces short intramolecular contacts between two hydrogen atoms on the N-methyl groups, and the electronegative O1 [H10c-O1 2.21 Å] and S1 [H11a-S1 2.66 Å] atoms.

The thiocarbamoyl moiety is diverted from the *ortho*-substituent, such that the aromatic and thiocarbamoyl fragments are not coplanar. This results in a close C1-S1 contact (3.00 Å), which is a requisite for the thermal rearrangement to occur. An ORTEP view of **4** at the 40% probability level is presented in Figure 1. Selected bond lengths and angles for compounds **4**, **5**, and **8** are listed in Table 2.

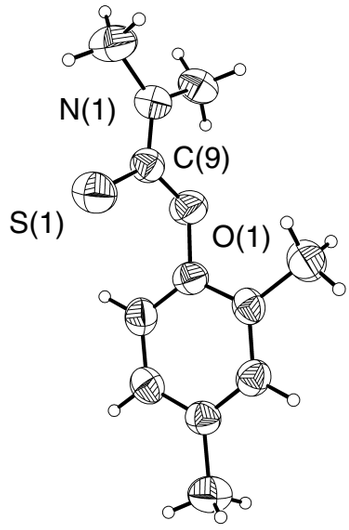


Figure 1. ORTEP view of **4**.

Although we were not able to obtain the crystal structure of the corresponding *S*-arylthiocarbamate **7** for comparison of the geometric parameters with those of **4**, we determined the solid state structures of *O*- and *S*-arylthiocarbamates **5** and **8**, which possess a *tert*-butyl *ortho*-substituent. Compounds **5** and **8** crystallize in the orthorhombic space group Pbca with different cell dimensions. The C12-S1 bond distance of **5** at 1.660(3) Å is comparable to that of related *O*-arylthiocarbamates.[8,10] The presence of the large sulfur atom in both *O*-thiocarbamates is likely responsible for the relatively small N-C-O angles of **4** [109.7(2)°], and **5** [110.3(2)°]. As in compound **4**, the thiocarbamoyl group of **5** has π-bonding contributions from the N and O lone pairs, as evidenced in the bond angles around N1 [C12-N1-C13 121.4(2)°, C12-N1-C14 123.1(2)°, C13-N1-C14 115.5(2)°] and O1 [C1-O1-C12 121.8(2)°].

Short intramolecular contacts, which are attributed to the planarity of the thiocarbamoyl group, are also present in the solid state structure of **5** [H14a-O1 2.20 Å, and H13c-S1 2.52 Å]. As in **4**, the thiocarbamoyl fragment of **5** is directed away from the *tert*-butyl substituent. This allows the S1 atom to make a close contact with the C1 atom (3.05 Å), which is directly involved in the rearrangement reaction.

In compound **8**, the carbonyl C12-O1 bond length of 1.210(2) Å is comparable to that of related *S*-aryl-thiocarbamates, and it further proves the thermal rearrangement of the O and S atoms. As in the case of **5**, the *S*-thiocarbamoyl fragment is planar, and directed away from the bulky *ortho*-substituent. A considerable amount of steric repulsion arises from the presence of the sulfur atom

Table 1. Crystal and refinement data for compounds **4**, **5** and **8**

	4	**5**	**8**
Formula	$C_{11}H_{15}NOS$	$C_{14}H_{21}NOS$	$C_{14}H_{21}NOS$
Formula weight	209.30	251.38	251.38
F(000)	448	1088	1088
Crystal size (mm)	0.24×0.19×0.04	0.36×0.26×0.22	0.45×0.10×0.10
Crystal habit	Prism	Prism	Prism
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$	*Pbca*	*Pbca*
a (Å)	9.135(1)	12.8815(9)	8.3186(8)
b (Å)	10.278(1)	12.5431(9)	13.3500(13)
c (Å)	13.147(2)	18.0191(13)	25.895(3)
α (°)	90	90	90
β (°)	110.338(2)	90	90
γ (°)	90	90	90
V (Å^3)	1157.4(2)	2911.4(4)	2875.8(5)
Z	4	8	8
ρ_{calc} (g cm^{-3})	1.201	1.147	1.161
μ (mm^{-1})	0.249	0.208	0.211
Radiation MoKα (Å)	0.71073	0.71073	0.71073
Diffractometer	Bruker Smart	Bruker Smart	Bruker Smart
θ min/max (°)	2.38/24.99	2.26/25.00	1.57/25.00
Reflections collected	9232	22080	21868
Data/restr/parameters	2031/0/131	2569/0/160	2530/0/160
Absorption correction	None	None	None
R_{int}	0.0653	0.0529	0.0613
R	0.0471	0.0562	0.0405
R_w	0.0965	0.1356	0.0912
Goodness-of-fit on F^2	*0.910*	*0.959*	*0.935*
Max/min peaks (e Å^{-3})	0.227/-0.135	0.307/-0.179	0.206/-0.155

directly bound to the aromatic ring in a position adjacent to the *tert*-butyl group. This is clearly reflected in the widening of the S1-C1-C2 [124.6(2)°] bond angle relative to the S1-C1-C6 [115.3(2)°] angle.

Despite the planar nature of the thiocarbamoyl group, and the bond angles around the N1 atom [C12-N1-C13 118.2(2)°, C12-N1-C14 125.0(2)°, C13-N1-C14 116.6(2)°], which correspond to sp^2-hybridization, the contribution of the S atom to the π-system does not appear to be significant based on the small bond angle [C1-S1-C12 99.9(1)°]. Short intramolecular contacts are once again present due to the planarity of the thiocarbamoyl moiety [H13c-O1 2.29 Å, and H14c-S1 2.37 Å], which enforces the proximity of C13 and C14 to the O1 and S1 atoms, respectively. A list of selected bond lengths and angles for all compounds is presented in Table 2, and ORTEP diagrams of **5** and **8** are shown in Figures 2 and 3, respectively.

Table 2. Selected bond distances (Å) and bond angles (°) for **4**, **5** and **8**

Compound **4**			
S1-C9	1.651(3)	C9-O1-C1	121.0(2)
O1-C9	1.357(3)	N1-C9-O1	109.7(2)
O1-C1	1.408(3)	N1-C9-S1	126.7(2)
N1-C9	1.322(3)	O1-C9-S1	123.6(2)
Compound **5**			
S1-C12	1.660(3)	C12-O1-C1	121.8(2)
O1-C12	1.363(3)	N1-C12-O1	110.2(2)
O1-C1	1.407(3)	N1-C12-S1	125.2(2)
N1-C12	1.321(3)	O1-C12-S1	124.5(2)
Compound **8**			
O1-C12	1.210(2)	C1-S1-C12	99.9(1)
S1-C12	1.802(2)	O1-C12-N1	124.4(2)
S1-C1	1.780(2)	O1-C12-S1	122.0(2)
N1-C12	1.341(3)	N1-C12-S1	113.6(2)

Conclusions

We have prepared and characterized new *O*-aryl and *S*-arylthiocarbamates which provide the entry point into

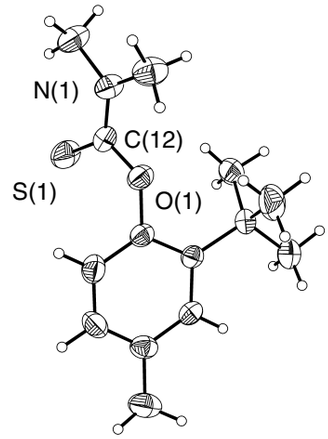


Figure 2. ORTEP view of **5**.

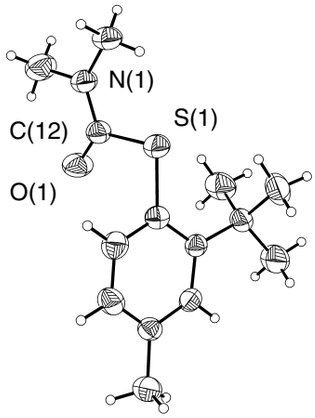


Figure 3. ORTEP view of **8**.

the synthesis of 2,4-disubstituted thiols. Of the latter compounds, **11** and **12** are thiophenols that feature bulky substituents in the 2-position, which have not previously been reported perhaps due to the difficulty in their preparation. These thiols may prove useful as sterically encumbered thiolate ligands towards transition metals, and thus we are currently undertaking their synthesis on a larger scale. Having one of the activated *ortho*-positions available, this series of thiophenols can be incorporated into more complex structures in polydentate sulfur-based ligands with varying degrees of steric hindrance, depending on the identity of the substituent on the 2-position.[11]

Experimental

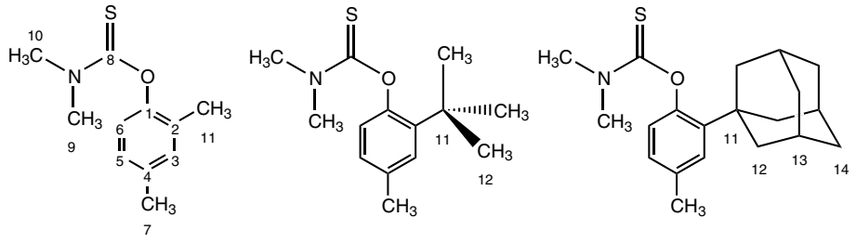
General methods

THF and dimethoxyethane were dried with sodium/benzophenone, and distilled under a nitrogen atmosphere. All other solvents were used as received from commercial suppliers. 2,4-dimethylphenol (**1**), 2-*tert*-butyl-4-methylphenol (**2**), 2-(1-adamantyl)-4-methylphenol (**3**), sodium hydride, and *N*,*N*-dimethylthiocarbamoyl chloride were purchased from Aldrich Chemical Co., and were used without further purification. IR spectra were obtained as chloroform solutions with a Perkin-Elmer 203-B spectrophotometer in the range 4000-400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL Eclipse spectrometer at 20 °C operating at 300 and 75 MHz respectively. Chemical shifts were reported using $Si(CH_3)_4$ as an internal standard. Electron-ionization mass spectrometry measurements were obtained with a JEOL JMS-AX505HA spectrometer. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN).

Synthesis of organosulfur compounds

For each kind of compound, *i. e. O*-arylthiocarbamate, *S*-arylthiocarbamate, and thiophenol, a detailed synthetic procedure is exemplified. The peaks that were specifically assigned in the NMR spectra are based on the numbering presented in Scheme 2.

*2,4-$Me_2C_6H_3OC(S)NMe_2$ (**4**).* In a two-necked round bottom flask equipped with a reflux condenser was dissolved 2,4-dimethylphenol (2.00 g, 16.40 mmol) in 75 mL of anhydrous dimethoxyethane under a nitrogen atmosphere. While the colorless solution was being vigorously stirred, solid NaH (0.43 g, 18.00 mmol) was added in small portions. Evolution of gas was observed (H_2), and the reaction mixture was allowed to stir until gas evolution subsided. *N*,*N*-dimethylthiocarbamoyl chloride (2.22 g, 18.00 mmol) was then added, and the mixture was heated to reflux for 24 h. After cooling to room temperature, the mixture was quenched with 30 mL of water, and the organic phase was diluted with 30 mL of diethylether. The phases were separated with a separatory funnel, and the aqueous phase was washed with 3×20 mL of diethylether. The combined organic phases were washed with distilled water (30 mL), a saturated Na_2CO_3 solution (30 mL), and were finally dried with anhydrous Na_2SO_4. The crude yellow solid obtained after filtration and evaporation of volatile materials was purified by column chromatography on silica gel by eluting with CH_2Cl_2; colorless crystals, (1.72 g, 50%); mp 59-62 °C; IR ($CHCl_3$) ν_{max}/cm^{-1}: 2987, 2928, 2870, 1536 (C=S), 1499, 1398, 1291, 1194, 1144; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.03 (d, ^{3}J 7.68 Hz, 1 H, H_5), 7.01 (s, 1 H, H_3), 6.86 (d, ^{3}J 7.68 Hz, 1 H, H_6), 3.45 (s, 3 H, NCH_3), 3.34 (s, 3 H, NCH_3), 2.32 (s, 3 H,



Scheme 2. Numbering scheme employed in NMR assignments.

ArCH_3), 2.15 (s, 3 H, ArCH_3); $^{13}C\{^1H\}$ NMR ($CHCl_3$, 75 MHz): δ 187.44 (C_8), 150.37 (Ar), 135.62 (Ar), 131.67 (Ar), 130.29 (Ar), 127.33 (Ar), 122.57 (Ar), 43.25 (NCH_3), 38.50 (NCH_3), 20.93 (ArCH_3), 16.26 (ArCH_3); *m/z* 209 (M^+, 68%), 137 (24), 121 (11), 105 (14), 88 (100), 72 (87). Found: C, 63.55; H, 7.60; N, 6.54. Calc. for $C_{11}H_{15}NOS$: C, 63.12; H, 7.22; N, 6.69%.

*2-^{t}Bu-4-MeC_6H_3OC(S)NMe_2 (**5**)*. Colorless crystals, (2.18 g, 53%); mp 62-64 °C; IR ($CHCl_3$) ν_{max}/cm^{-1}: 3014, 2962, 2866, 1710, 1526 (C=S), 1487, 1392, 1363, 1288, 1143, 1085, 1053, 925, 878; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.18 (d, ^4J 2.07 Hz, 1 H, H_3), 7.03 (dd, ^3J 8.25 Hz, ^4J 2.07 Hz, 1 H, H_5), 6.9 (d, ^3J 8.25 Hz, 1 H, H_6), 3.49 (s, 3 H, NCH_3), 3.39 (s, 3 H, NCH_3), 2.34 (s, 3 H, ArCH_3), 1.33 (s, 9 H, ^{t}Bu); $^{13}C\{^1H\}$ NMR ($CHCl_3$, 75 MHz): δ 188.18 (C_8), 150.31 (Ar), 140.59 (Ar), 135.06 (Ar), 127.84 (Ar), 127.02 (Ar), 125.08 (Ar), 43.36 (NCH_3), 38.82 (NCH_3), 34.44 (ArCH_3), 30.76 (C_{12}), 21.29 (C_{11}); *m/z* 251 (M^+, 31%), 194 (28), 163 (1), 145 (6), 88 (100), 72 (47). Found: C, 67.09; H, 8.53; N, 5.22. Calc. for $C_{14}H_{21}NOS$: C, 66.89; H, 8.42; N, 5.57%.

*2-(1-Ad)-4-MeC_6H_3OC(S)NMe_2 (**6**)*. Colorless crystals, (4.92 g, 91%); mp 169-172 °C; IR ($CHCl_3$) ν_{max}/cm^{-1}: 2905, 2851, 2739, 2668, 1553 (C=S), 1493, 1451, 1392, 1285, 1249, 1196, 1133, 1044, 813, 757; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.15 (s, 1 H, H_3), 6.99 (d, ^3J 7.98 Hz, 1 H, H_5), 6.88 (d, ^3J 7.98 Hz, 1 H, H_6), 3.51 (s, 3 H, NCH_3), 3.42 (s, 3 H, NCH_3), 2.34 (s, 3 H, ArCH_3), 2.07 (s, 3 H, H_{13}) 2.02 (s, 6 H, Ad), 1.73 (m, 6 H, Ad); $^{13}C\{^1H\}$ NMR ($CHCl_3$, 75 MHz): δ 188.28 (C_8), 150.62 (Ar), 140.74 (Ar), 135.21 (Ar), 127.79 (Ar), 126.85 (Ar), 125.35 (Ar), 43.51 (NCH_3), 41.62 (Ad), 38.97 (NCH_3), 37.04 (Ad), 36.72 (ArCH_3), 29.01 (Ad), 21.41 (Ad); *m/z* 330 (M^+, 96%), 257 (21), 88 (100), 72 (48). Found: C, 72.67; H, 8.51; N, 3.98. Calc. for $C_{20}H_{27}NOS$: C, 72.90; H, 8.26; N, 4.25%.

*2,4-$Me_2C_6H_3$SC(O)NMe_2 (**7**)*. Yellow crystals, (1.23 g, 34%); mp 33-34 °C; IR ($CHCl_3$) ν_{max}/cm^{-1}: 2926, 2827, 1654 (C=O), 1479, 1441, 1367, 1261, 1100, 1057; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.34 (d, ^3J 7.71 Hz, 1 H, H_5), 7.11 (s, 1 H, H_3), 7.00 (d, ^3J 7.71 Hz, 1 H, H_6), 3.11 (br, s, 3 H, NCH_3), 3.02 (br, s, 3 H, NCH_3), 2.37 (s, 3 H, ArCH_3), 2.32 (s, 3 H, ArCH_3); $^{13}C\{^1H\}$ NMR ($CHCl_3$, 75 MHz): δ 166.83 (C_8), 142.74 (Ar), 140.01 (Ar), 136.97 (Ar), 131.46 (Ar), 127.24 (Ar), 124.66 (Ar), 36.88 (NCH_3), 21.21 (ArCH_3), 20.94 (ArCH_3); *m/z* 209 (M^+, 10%), 80 (40), 137 (28), 124 (60), 105 (36), 91 (65), 83 (36), 71 (48), 57 (100), 43 (79), 28 (65), 18 (35). Found: C, 63.66; H, 7.06; N, 6.53. Calc. for $C_{11}H_{15}NOS$: C, 63.12; H, 7.22; N, 6.69%.

*2-^{t}Bu-4-MeC_6H_3SC(O)NMe_2 (**8**)*. Colorless crystals, (1.48 g, 46%); mp 79-80 °C; IR ($CHCl_3$) ν_{max}/cm^{-1}: 3010, 2957, 2862, 1653 (C=O), 1594, 1474, 1363, 1259, 1096, 1041, 907; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.34 (d, ^3J 7.98 Hz, 1 H, H_6), 7.27 (s, 1 H, H_3), 7.04 (d, ^3J 7.98 Hz, 1 H, H_5), 3.08 (br, s, 6 H, NCH_3), 2.35 (s, 3 H, Ar), 1.46 (s, 9 H, ^{t}Bu); $^{13}C\{^1H\}$ NMR (75 MHz, $CHCl_3$): δ 167.57 (C_8), 152.52 (Ar), 141.26 (Ar), 139.41 (Ar), 127.83 (Ar), 127.32 (Ar), 123.95 (Ar), 36.99 (NCH_3), 36.30 (ArCH_3), 30.97 (C_{12}), 21.65 (C_{11}); *m/z* 251 (M^+, 25%), 194 (19), 179 (3), 72 (100). Found: C, 67.30; H, 8.69; N, 5.24. Calc. for $C_{14}H_{21}NOS$: C, 66.89; H, 8.42; N, 5.57%.

*2-(1-Ad)-4-MeC_6H_3SC(O)NMe_2 (**9**)*. Solid **6** (0.25 g, 0.76 mmol) was dried under vacuum in a Schlenk flask for 1 h. The flask was immersed in a sand bath and heated to 310 °C for 2 h, keeping the top of the flask wrapped with aluminum foil to maintain a uniform temperature. After cooling to room temperature, the products were dissolved in 20 mL CH_2Cl_2, filtered, and concentrated by evaporation of volatile materials. The product was separated from starting material by column chromatography by eluting with CH_2Cl_2. In this manner 0.07 g of **6** were recovered and recycled, and **9** was obtained as an off-white solid (0.06 g, 23%); mp 134-135 °C; IR ($CHCl_3$) ν_{max}/cm^{-1}: 3011, 2908, 2852, 1710, 1655 (C=O), 1598, 1451, 1406, 1365, 1261, 1170, 1100, 1066, 1029, 910; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.24 (d, ^3J 7.68 Hz, 1 H, H_6), 7.13 (d, ^4J 1.38 Hz, 1 H, H_3), 6.94 (dd, ^3J 7.68 Hz, ^4J 1.38 Hz, 1 H, H_5), 3.02 (br, s, 6 H, NCH_3), 2.28 (s, 3 H, ArCH_3), 2.12 (s, 6 H, Ad), 2.02 (s, 3 H, H_{13}), 1.69 (s, 6 H, Ad); $^{13}C\{^1H\}$ NMR ($CHCl_3$, 75 MHz): δ 166.64 (C_8), 151.30 (Ar), 140.51 (Ar), 138.42 (Ar), 126.90 (Ar), 126.09 (Ar), 122.75 (Ar), 40.37 (NCH_3), 37.21 (ArCH_3), 36.00 (Ad), 35.79 (Ad), 28.21 (Ad), 20.64 (Ad); *m/z* 330 (M^+, 14%), 257 (33), 194 (13), 72 (100); Found: C, 73.22; H, 7.96; N, 4.03. Calc. for $C_{20}H_{27}NOS$: C, 72.90; H, 8.26; N, 4.25%.

*2,4-$Me_2C_6H_3SH$ (**10**)*. Yellow liquid, (1.23 g, 55%); *m/z* 209 (M^+, 10%), 80 (40), 137 (28), 124 (60), 105 (36), 91 (65), 83 (36), 71 (48), 57 (100), 43 (79), 28 (65), 18 (35).

*2-^{t}Bu-4-MeC_6H_3SH (**11**)*. In a Schlenk flask under a nitrogen atmosphere compound **8** (1.46 g, 5.80 mmol) was dissolved in 25 mL of anhydrous THF, and the flask was cooled in an ice bath. Solid $LiAlH_4$ (0.44 g, 11.60 mmol) was added in small portions while the solution was vigorously stirred. The reaction mixture was stirred for 1 h while warmed to room temperature, and then heated to reflux overnight. After cooling to 0 °C, the mixture was quenched with 3 mol L^{-1} HCl until a pH of 2 was reached, and the organic phase was isolated with a separatory funnel. The aqueous phase was extracted with 3×20 mL of diethylether, and the combined organic phases were washed with distilled water, dried with Na_2SO_4, filtered, and concentrated to dryness to obtain pure **11** (0.66 g, 63%); yellow oil; IR ($CHCl_3$) ν_{max}/cm^{-1}: 2962, 2918, 2871, 2567 (S-H), 1598,1477, 1456, 1396, 1364, 1251, 1214, 1121, 1049, 1021, 931, 901, 807, 758; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.17 (s, 1 H, H_3), 7.12 (d, ^3J 7.68 Hz, 1 H, H_6), 6.84

(d, ^3J 7.68 Hz, 1 H, H_5), 3.52 (s, 1 H, S*H*), 2.28 (s, 3 H, ArCH_3), 1.46 (s, 9 H, ^{t}Bu); $^{13}C\{^1H\}$ NMR ($CHCl_3$, 75 MHz): δ 147.29 (Ar), 135.32 (Ar), 133.55 (Ar), 127.92 (Ar), 127.17 (Ar), 126.39 (Ar), 35.98 (ArCH_3), 29.78 (C_{12}), 21.27 (C_{11}); *m/z* 358 ($[M_2]^+$, 100%), 180 (M^+, 12), 163 (43), 148 (7), 137 (13), 123 (6), 105 (4), 55 (7). Found: C, 73.15; H, 9.11. Calc. for $C_{11}H_{16}S$: C, 73.28; H, 8.94%.

*2-(1-Ad)-4-MeC_6H_3SH (**12**)*. Colorless thick oil, (0.03 g, 68%); IR ($CHCl_3$) ν_{max}/cm^{-1}: 2906, 2850, 2677, 2564 (S-H), 1599, 1450, 1372, 1315, 1260, 1097, 1027, 908, 871, 804; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.11 (s, 1 H, H_3), 7.09 (d, ^3J 7.98 Hz, 1 H, H_6), 6.83 (d, ^3J 7.98 Hz, 1 H, H_5), 3.57 (s, 1 H, S*H*), 2.28 (s, 3 H, H_7) 2.19 (s, 6 H, Ad), 2.12 (s, 3 H, H_{13}), 1.78 (s, 6 H, Ad); $^{13}C\{^1H\}$ NMR ($CHCl_3$, 75 MHz): δ 147.42 (Ar), 135.33 (Ar), 133.79 (Ar), 127.94 (Ar), 126.96 (Ar), 126.00 (Ar), 40.14 (Ad), 37.74 (ArCH_3), 36.78 (Ad), 29.08 (Ad), 21.16 (Ad); *m/z* 514 ($[M_2]^+$, 8%), 258 (M^+, 100), 201 (11), 161 (15), 149 (13), 135 (8), 91 (6), 79 (6), 55 (5); Found: C, 78.88; H, 8.97. Calc. for $C_{17}H_{22}S$: C, 79.01; H, 8.58%.

*Crystallographic data collection and structure determination of compounds **4**, **5**, and **8***

Single crystals were mounted at room temperature on a Bruker SMART diffractometer equipped with an Apex CCD area detector. Frames were collected by omega scans, and integrated with the Bruker SAINT software package[12] using the appropriate unit cell. The structures were solved using the SHELXS-97 program,[13] and refined by full-matrix least-squares on F^2 with the SHELXL-97 program.[14] Hydrogen atoms were calculated in ideal positions, and refined as riding, with a fixed $U_{iso} = 1.2\ U_{eq}$ of the parent atom, and with C-H distances in the range 0.93-0.97 Å. All non-hydrogen atoms were refined anisotropically.

Acknowledgment

The authors wish to thank DGAPA-UNAM for financial support through project IN247402, Professor T. Don Tilley for a generous gift of 2-(1-adamantyl)-4-methylphenol, and Simón Hernández-Ortega for crystallographic work.

Supplementary Information

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 253728-253730. Copies of the data can be obtained, free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK ; fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk).

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Received: October 29, 2004
Published on the web: April 12, 2005