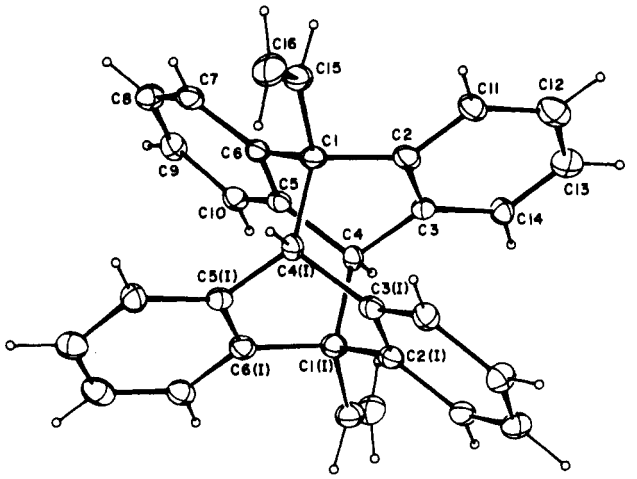

Figure 1. X-ray crystal structure of 9-vinylanthracene dimer. Hydrogen atoms are not labeled for clarity. The roman numeral I refers to the equivalent position 1-x, 1-y, 1-z relative to the reference molecule at x, y, z.

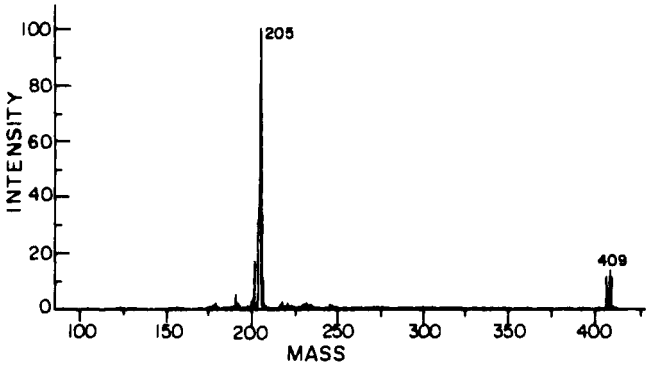

Figure 2. Mass spectrum (methane CI) of 9-vinylanthracene dimer (only H^+ (monomer) and H^+ (dimer) peaks are shown).

through an angle of 2 × 23°, again similar to the dimer of 9-anthraldehyde.[5] This dimer, like other dimers of anthracene, is unstable at higher temperatures (>150 °C) and is converted to the monomeric species upon heating. Therefore, during mass spectral analyses the signal corresponding to the monomeric mass is predominantly present. However, careful analysis and amplification of signals revealed a small peak at m/e 409 (see Figure 2) corresponding to the protonated dimeric mass.

Acknowledgment. Continuing support from Natural Sciences and Engineering Council of Canada (NSERC) is gratefully acknowledged.

(5) Ehrenberg, M. *Acta Crystallogr.* **1968**, *B24*, 1123.
(6) Sheldrick, G. M. *SHELXS86, A program for crystal structure determination*; University of Gottingen: F.R.G., 1986.
(7) Sheldrick, G. M. *SHELX76, A program for crystal structure determination*; University of Cambridge: England, 1976.
(8) The dimer is insoluble in most solvents for UV analysis. ^1H NMR data in $CDCl_3$: (400 MHz) δ 4.86 (s, 2 H), 5.95 (d, J = 11.02 Hz, 2 H), 6.15 (d, J = 17.58 Hz, 2 H), 6.39 (q, J = 17.7 Hz, 2 H), 6.81 (m, 12 H), 6.99 (m, 4 H). ^{13}C NMR data δ 53.57, 58.56, 115.82, 125.27, 125.62, 126.04, 127.71, 142.36, 142.39, 145.61.
(9) Crystal data: $C_{32}H_{24}$, M = 408.5, monoclinic, space group $P2_1/c$, a = 8.085 (2) Å, b = 13.224 (3) Å, c = 10.533 (3) Å, β = 109.92 (2)°, U = 1058.8 Å^3, Z = 2, D_c = 1.29 g cm^{-3}, λ(Mo Kα) = 0.71073 Å, μ = 0.68 cm^{-1}, F(000) = 432, room temperature, R = 0.042 (R_w = 0.038) for 862 reflections (measured on a CAD4 diffractometer) with $I > 3\sigma(I)$. The crystals were grown by slow evaporation of solvent from benzene solution. The structure was solved by direct methods[6] and reduced by full-matrix least squares.[7] Carbon atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the —CH=CH_2 group and the hydrogen bonded to the sp^3 hybridized carbon were refined with isotropic thermal parameters. All other hydrogen atoms were included in the refinement as riding atoms with d(C–H) of 0.95 Å and a general thermal parameter for these atoms refined to U = 0.045 (3) Å^2.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles (7 pages). Ordering information is given on any current masthead page.

Preparation of Thiophenols from Unactivated Aryl Chlorides and Sodium Alkanethiolates in *N*-Methyl-2-pyrrolidone

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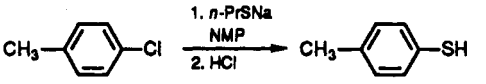
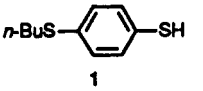
Thiophenols can be prepared in high yield by nucleophilic substitution reactions of unactivated and deactivated aryl chlorides with sodium alkanethiolates in *N*-methyl-2-pyrrolidone (NMP). The one-pot method involves the reactions shown in Scheme I.

These reactions have been previously carried out in hexamethylphosphoramide (HMPA)[1] and *N*,*N*-dimethylformamide (DMF)[2] with more reactive aryl chlorides. However, HMPA has the disadvantages of carcinogenic properties and high cost. Our work has shown that using DMF with deactivated aryl chlorides such as 4-chlorotoluene gave poor results. After being refluxed for 20 h in DMF, most of the 4-chlorotoluene was unreacted and the yield of 4-methylbenzenethiol was only 16%. It has been found that the yield of thiophenols can be dramatically improved if NMP is used as solvent. Reaction of 4-chlorotoluene with sodium propanethiolate or sodium butanethiolate (4 mol equiv) in NMP at reflux gave 4-methylbenzenethiol in 90–96% yield as determined by GC. Di-*n*-propyl sulfide or di-*n*-butyl sulfide was produced as a coproduct.



Reaction of 2-chlorotoluene with excess sodium butanethiolate under the same conditions gave a 96% yield of 2-methylbenzenethiol. Any steric hindrance in 2-chlorotoluene was apparently not a problem in the reactions. Application of this method to the more reactive chlorobenzene also resulted in a high yield (92%) of thiophenol. The reaction time and temperature were less for chlorobenzene than for 4-chloro- or 2-chlorotoluene.

Attempts to prepare 1,4-benzenedithiol from 1,4-dichlorobenzene failed. Instead, compound **1** was produced (94% yield) apparently because the sodium salt of this compound fails to undergo further reaction with excess *n*-BuSNa (6 mol equiv) in NMP.



1

In the aforementioned reactions, sodium alkanethiolates derived from primary alkyl mercaptans were used. If sodium alkanethiolates from tertiary alkyl mercaptans were used, the second reaction in Scheme I was not possible due to steric factors, so aryl alkyl sulfides were obtained instead

(1) Testaferri, L.; Tingoli, M.; Tiecco, M. *Tetrahedron Lett.* **1980**, *21*, 3099–3100.
(2) Testaferri, L.; Tiecco, M.; Tingoli, M.; Chianelli, D.; Montanucci, M. *Synthesis* **1983**, 751–755.

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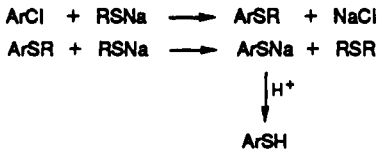
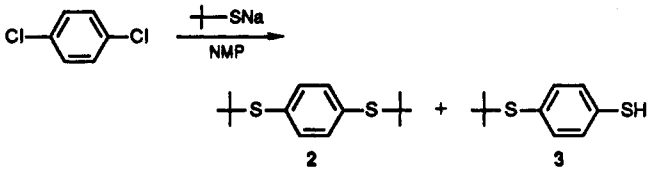
Scheme I



of thiophenols. Reaction of 1,4-dichlorobenzene with the sodium salt of *tert*-butyl mercaptan gave compounds **2** and **3** in yields of 89 and 7%, respectively. Thiophenol **3** was probably formed from **2** by elimination of isobutene rather than by nucleophilic substitution since no di-*tert*-butyl sulfide was observed.



2 **3**

In all the reactions of aryl chlorides with sodium alkanethiolates, the thiolate was prepared by reaction of an alkyl mercaptan with sodium hydroxide in NMP. Before addition of the aryl chloride, it was necessary to remove the water that was formed since the reaction rates were too slow with water present. This was accomplished by addition of toluene and azeotropic distillation of water with toluene. In small-scale reactions, the sodium alkanethiolates can be produced using sodium hydride so water is not formed and the azeotropic distillation step can be avoided.

Experimental Section

4-Methylbenzenethiol. To a 3-L, three-necked flask equipped with a N_2 inlet, thermowell, magnetic stirring bar, and Dean Stark trap with condenser were added 900 mL of NMP, 96 g (2.4 mol) of sodium hydroxide, and 183 g (218 mL, 2.4 mol) of *n*-propyl mercaptan. The mixture was stirred and heated at 40 °C until the NaOH dissolved. Then, 375 mL of toluene was added and the mixture was heated at reflux with water being removed by the Dean Stark trap. After all the water (~45 mL) was removed, the toluene (375 mL) was distilled off. An extra 25 mL of liquid was distilled off to ensure complete removal of toluene. The reaction flask was allowed to cool almost to room temperature. The Dean Stark trap was removed, but the condensor was retained. Then, 76.0 g (0.60 mol) of 4-chlorotoluene was added and the solution was refluxed (~186 °C) overnight (20 h). The solution was cooled to room temperature. A solution of 225 mL of concentrated hydrochloric acid and 225 mL of water was added slowly with stirring and cooling until the mixture reached pH 3. After addition of an additional 450 mL of water, the mixture was extracted with 900 mL of ethyl ether. The aqueous layer was extracted a second time with 450 mL of ether. The combined ether extract was washed with three 150-mL portions of water, dried with anhydrous sodium sulfate, and evaporated under reduced pressure to give 172 g of liquid. GC analysis (20 in. × $^1/_8$ in. 2% OV-101 with programmed temperature rise of 15 °C/min starting at 50 °C) of the liquid showed that it contained 41.6% 4-methylbenzenethiol and 30.7% di-*n*-propyl sulfide. The yield of 4-methylbenzenethiol by GC was 96%. The liquid was fractionally distilled on a column containing high-efficiency stainless steel packing. The isolated yield of 4-methylbenzenethiol (bp 109–110 °C (50 Torr)) was 87%. All products were identified by comparison with authentic materials by IR, NMR, and GC retention time.

When the above reaction was carried out with *n*-butyl mercaptan instead of *n*-propyl mercaptan, the yield (GC) of 4-methylbenzenethiol was 90%.

2-Methylbenzenethiol. The reaction was carried out in the same way as for 4-methylbenzenethiol except one-third scale, and *n*-butyl mercaptan was used instead of *n*-propyl mercaptan. The amount of 2-chlorotoluene used was 25.3 g (0.20 mol). Workup gave 67.2 g of a liquid that was shown by GC analysis to contain 35.3% of 2-methylbenzenethiol and 44.0% of di-*n*-butyl sulfide. The yield of 2-methylbenzenethiol by GC was 96%. All products were identified by comparison with authentic materials.

Thiophenol. The reaction procedure was the same as that described for 4-methylbenzenethiol except at one-third scale, with use of chlorobenzene. The reaction temperature was 172 °C, and the reaction time was 9 h. The yield (GC) of thiophenol was 92%.

4-(*n*-Butylthio)benzenethiol (1). The procedure was the same as that described for 4-methylbenzenethiol except on a smaller scale, using 0.133 mol of 1,4-dichlorobenzene and 0.80 mol of sodium butanethiolate derived from *n*-butyl mercaptan. The reflux temperature was 185–190 °C and the reaction time was 9 h. After the workup described previously, GC analysis of the crude product showed the yield was 94%.

Compound **1** was isolated by extraction of an ether solution of the crude product with 10% aqueous NaOH solution. The aqueous layer was acidified with 4 M HCl solution and then extracted with ether. The ether extract was washed two times with water, dried over anhydrous sodium sulfate, evaporated, and distilled: bp 162–165 °C (15 Torr) (lit.[3] bp 165 °C (16 Torr)); IR (neat) 1475, 1388, 1107, 1009, 803, 484 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.87 (t, 3 H, J = 7.2 Hz), 1.12–1.78 (m, 4 H), 2.81 (t, 2 H, J = 7.0 Hz), 3.53 (s, 1 H), 7.02–7.53 (m, 4 H). Anal. Calcd for $C_{10}H_{14}S_2$: C, 60.55; H, 7.12; S, 32.33. Found: C, 60.84; H, 7.01; S, 32.01.

1,4-Bis(*tert*-butylthio)benzene (2) and 4-(*tert*-Butylthio)benzenethiol (3). The procedure was the same as that described previously, except on a smaller scale, with use of 0.40 mol of 1,4-dichlorobenzene and 1.6 mol of sodium alkanethiolate derived from *tert*-butyl mercaptan. The reaction mixture was heated at 150 °C rather than refluxed and the reaction time was 6.5 h. After workup, 100.9 g of a white solid was obtained. GC analysis of the solid showed it contained 89.8% of **2** and 5.5% of **3**. The yields (GC) of **2** and **3** were 89 and 7%, respectively.

The two compounds were separated by the extraction procedure described for **1**. Compound **2** was obtained as white crystals: mp 111–113 °C (lit.[4] mp 112–113 °C); IR (neat) 1462, 1367, 1171, 832, 578, 508 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.31 (s, 18 H), 7.52 (s, 4 H); MS m/z 254 (M^+), 142 (base), 57, 41. Anal. Calcd for $C_{14}H_{22}S_2$: C, 66.08; H, 8.72; S, 25.20. Found: C, 65.98; H, 8.65; S, 24.98.

Compound **3** was a pale yellow liquid: IR (neat) 1473, 1360, 1164, 1104, 1011, 814, 499 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.24 (s, 9 H), 3.52 (s, 1 H), 7.12–7.50 (m, 4 H); MS m/z 198 (M^+), 142 (base), 78, 57. Anal. Calcd for $C_{10}H_{14}S_2$: C, 60.55; H, 7.12; S, 32.33. Found: C, 60.56; H, 7.04; S, 32.16.

Acknowledgment. I wish to thank Marilyn G. McAfee for doing many of the experiments.

(3) Protiva, M.; Rajsner, M.; Adlerova, E.; Scidlova, V.; Vejdelek, Z. J. *Collect. Czech. Chem. Commun.* **1964**, *29*, 2161–2181.
(4) Cogolli, P.; Testaferri, L.; Tingoli, M.; Tiecco, M. *J. Org. Chem.* **1979**, *44*, 2636–2642.

Effective Transformation of Unactivated Alkynes into Ketones or Acetals by Means of Au(III) Catalyst

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Hydration is one of the most useful functionalizations of simple alkynes, especially for the preparation of methyl ketones from terminal alkynes. Therefore, a variety of catalysts for this reaction have been extensively studied.[1-14]

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