DCC (487 mg, 2.36 mmol) in 10 mL of $CH_2Cl_2$. After the reaction mixture was stirred for 5 min, 50 μL of anhydrous pyridine in 1 mL of $CH_2Cl_2$ was added, stirring was continued at 0 °C for 1 h and then at room temperature for 1 h. TLC analysis (PhH–EtOAc) showed complete conversion of **3** ($R_f$ 0.3) to **5** ($R_f$ 0.53) during this period. The crude product was worked up by our general procedure.[3,4] Crystallization from acetone–petroleum ether gave 340 mg (80% yield) of **5**: mp 178–180 °C; UV 235 nm (ε 15400); IR 3525 (hydroxy), 1753 (ester), 1712 (C-20, C=O), 1670 (C-3, C=O), 1622 $cm^{-1}$ ($\Delta^4$); NMR ($CDCl_3$) δ 5.89 (s, 1, H-4), 5.14 (m, 1, H-6α), 4.50 (m, 1, H-11α), 4.17 (d, 2, $J$ = 5 Hz, H-21), 3.85 (s, 2, C-6β, $BrCH_2COO$), 1.57 (s, 3, H-19), 1.25 (d, 6, $J$ = 3, C-17/C-21, $C(CH_3)_2$), 0.95 (s, 3, H-18). Anal. Calcd for $C_{26}H_{35}O_7Br$: C, 57.89; H, 6.54; Br, 14.81. Found: C, 58.05; H, 6.74; Br, 14.62.

**6β-(Bromoacetoxy)-11β,17,21-trihydroxy-4-pregnene-3,20-dione (6).** A solution of **5** (350 mg, 0.65 mmol) in 4 mL of MeOH and 7 mL of 1:1 HOAc–$H_2O$ was heated at 52 °C for 5 h. TLC (PhH–EtOAc) showed progressive disappearance of **5** ($R_f$ 0.55) with formation of **6** ($R_f$ 0.08). After the reaction was complete, the solvent was evaporated and the residue was extracted with EtOAc. The EtOAc extract was washed with water, dried ($MgSO_4$), and filtered. Evaporation of the solvent from the filtrate left a solid residue which was crystallized from acetone–petroleum ether to give 160 mg of colorless crystals of **6**: mp 183–185 °C; UV 241 nm; IR 3440 (hydroxy), 1735 (ester), 1703 (C-20, C=O), 1677 (C-3, C=O), 1622 $cm^{-1}$ ($\Delta^4$); NMR ($CD_3CN$) δ 5.80 (s, 1, H-4), 5.40 (m, 1, H-6α), 4.35 (q, 2, $J$ = 5 Hz, H-21), [4.35 (m, 1, H-11α)], 3.95 (s, 2, C-6β, $BrCH_2COO$), 1.50 (s, 3, H-19), 0.85 (s, 3, H-18). Anal. Calcd for $C_{23}H_{31}O_7Br$: C, 55.32; H, 6.26; Br, 16.00. Found: C, 55.21; H, 6.44; Br, 16.16.

**6β,21-Bis(bromoacetoxy)-11β,17-dihydroxy-4-pregnene-3,20-dione (7).** A procedure for the synthesis of **7** from **6** was used which is similar to that described above for the synthesis of **5**. Thus, 250 mg (0.5 mmol) of **6** was converted to 225 mg of **7** (colorless needles from cyclohexane, mp 156–158 °C) which was found to be identical in all respects (TLC, UV, IR, NMR, and mmp) with **7** which had been obtained by direct bromoacetylation of **4**.

**6β-Acetoxy-11β,17,21-trihydroxy-4-pregnene-3,20-dione 17,21-Acetonide (9) from 3.** Compound **3** (106 mg, 0.25 mmol) was acetylated in a mixture of 0.4 mL of $Ac_2O$ in 2 mL of dry pyridine at room temperature. TLC (PhH–EtOAc) indicated complete conversion of **3** ($R_f$ 0.33) to **9** ($R_f$ 0.58) during 4 h. Recrystallization of the product from EtOAc–cyclohexane gave 60 mg of **9** with mp 195–199 °C (lit.[14] mp 207–211 °C). NMR and TLC agreed with the literature values.

**6β,21-Diacetoxy-11β,17-dihydroxy-4-pregnene-3,20-dione (8).** Starting with 77 mg (0.2 mmol) of **4**, a procedure similar to that used for the synthesis of **9** gave 50 mg of colorless needles from EtOAc–petroleum ether: mp 134–145 °C; UV 239 nm (ε 16100); IR 3260 (hydroxy), 1747 (ester), 1727 (C-20, C=O), 1660 (C-3, C=O), 1637 $cm^{-1}$ ($\Delta^4$). Anal. Calcd for $C_{25}H_{34}O_8$: C, 64.92; H, 7.41. Found: C, 65.01; H, 7.48.

**Reaction of 7 with 3α,20β-Hydroxysteroid Dehydrogenase.** To a solution of 0.5 μg (5 nmol) of 3α,20β-HSD in 5 mL of 0.05 M phosphate buffer at pH 6.0 and 25 °C was added 0.27 mg (500 nmol) of **7** in 200 μL of ethanol. At 30- to 60-min intervals, 3α or 20β enzyme activity was measured[9] in the 100-μL aliquots that were removed from the reaction mixture. Similar measurements were made on aliquots taken from an enzyme-control mixture which contained a quantity of **8** equivalent to **7** in the reaction mixture. The change in enzyme activity (calculated as a percent of enzyme activity in the control mixture) was plotted on a logarithmic scale as a function of time (Figure 1). The reactions of **6** or **7** with 3α,20β-HSD when carried out at pH 6.0 caused a time-dependent loss in enzyme catalytic activity which followed first-order kinetics (panel A, Figure 1). The reaction between **7** and 3α,20β-HSD at pH 7.0 was complicated by hydrolysis of **7** to **6**. This is reflected by the nonlinear logarithmic plot shown in panel B, Figure 1.

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**Registry No.** **1**, 50-23-7; **2**, 55388-47-1; **3**, 55388-50-6; **4**, 2242-98-0; **5**, 90295-95-7; **6**, 90295-96-8; **7**, 90320-60-8; **8**, 90295-97-9; **9**, 55388-51-7; 3α,20β-hydroxysteroid dehydrogenase, 72855-18-6.

## Reductive Cleavage of Aromatic Disulfides Using a Polymer-Supported Phosphine Reagent

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The use of polymeric reagents in organic synthesis has been the subject of substantial interest in recent years.[1] Among the several advantages offered by such reagents,[2] the one most frequently utilized is the ease of workup, often consisting of a simple filtration. This feature is particularly noteworthy when the reaction products are noxious or toxic and when they are unstable during lengthy workups. The reductive cleavage of disulfides to afford the corresponding thiols is certainly a reaction that could benefit substantially by application of these polymer-supported reagents due to the well-recognized noxious properties of the sulfur products. In addition, many of the thiol products are subject to air oxidation to regenerate the disulfides, a process inhibited by simplifying the workup procedure. With this goal in mind, we have developed a mild and high yield method for the reductive cleavage of a variety of disulfides to their corresponding thiols using a polymer-supported reagent.

The reductive cleavage of disulfides has been accomplished in a number of ways including reductions with $NaBH_4$,[3] $LiAlH_4$,[4] and Zn/acetic acid.[5] One method that appeared to be particularly attractive because of its mild conditions and high yields was the use of triphenylphosphine in aqueous organic solvents.[6] The yields of this reaction were sufficiently high to allow it to be used for quantitation of disulfides.[7] First described by Schönberg in the 1930s,[8] the reaction has been extensively studied and the mechanism carefully detailed.[9-11] As indicated in Scheme I, the first step involves a thiophilic attack by phosphorus to generate the aryl thiolate anion and the (arylthio)phosphonium cation, the latter undergoing hydrolysis in the second step to afford the second equivalent of thiol. The reaction is catalyzed by either acid or base.

**Scheme I**

$$Ar\text{–}S\text{–}S\text{–}Ar + Ph_3P \rightleftarrows Ar\text{–}S\text{–}P^+Ph_3 + ArS^-$$

$$Ar\text{–}S\text{–}P^+Ph_3 + H_2O \rightarrow ArS^- + 2H^+ + Ph_3PO$$

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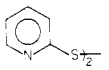
0022-3263/84/1949-2637$01.50/0 

**Table I. Reductive Cleavage of Aromatic Disulfides**

| | substd phenyl disulfide | disulfide mp, °C (lit.) | reactn conditns | yield of thiol, % | thiol mp, °C (lit.) |
|---|---|---|---|---|---|
| 1 | unsubstituted | 59–61 (60–61)[a] | 3 h, reflux | 76 | oil |
| 2 | 4-Cl | 71–73 (71–72)[a] | 2 h, 25 °C | 98 | 49–51 (52)[b] |
| 3 | 2,4,5-$Cl_3$ | 145–147 (146.5–147.5)[c] | 1 h, 25 °C | 93 | 107–112 (115–116)[d] |
| 4 | 3-$NO_2$ | 82–85 (80.5–82)[a] | 15 min, 25 °C | 96 | oil |
| 5 | 2-COOH | 286–290 (290–292)[a] | 7 h, reflux | 73[e] | 160–164 (165–168)[f] |
| 6 | 2-$COOCH_3$ | 134–136 (131.5–133.5)[a] | 24 h, reflux | 98 | oil |
| 7 | 4-$OCH_3$ | 42–45 (44–45)[a] | 6 h, reflux | 99 | oil |
| 8 | 4-$NH_2$ | 71–72 (77–77.5)[a] | 22 h, reflux | 97<br>73[g] | 32–38 (43–45)[h] |
| 9 | 4-$CH_3$ | 44–46 (44–46)[a] | 4 h, reflux | 93 | 39–42 (43.5–44)[i] |
| 10 |  | 57–60 (56–58)[j] | 15 min, 25 °C | 94 | 124–128 (127–129)[k] |

[a] See ref 9. [b] Fava, A.; Reichenbach, G.; Peron, U. *J. Am. Chem. Soc.* **1967**, *89*, 6696. [c] Lukashevich, V. O. *Dokl. Akad. Nauk SSSR* **1955**, *103*, 627. [d] Trompen, W. P.; Huisman, H. O. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 167. [e] Recrystallized yield. [f] Katz, L.; Karger, L. S.; Schroeder, W.; Cohen, M. S. *J. Org. Chem.* **1953**, *18*, 1380. [g] PLC yield. [h] Gilman, H.; Gainer, G. C. *J. Am. Chem. Soc.* **1949**, *71*, 1747. [i] Illuminati, G.; Linda, P.; Marino, G. *Ibid.* **1967**, *89*, 3521. [j] Danehy, J. P.; Elia, V. J.; Lavelle, C. J. *J. Org. Chem.* **1971**, *36*, 1003. [k] Evans, R. F.; Brown, H. C. *Ibid.* **1962**, *27*, 1329.

While the reaction as described is quite clean and affords high yields, it does necessitate the separation of the thiol from the triphenylphosphine oxide byproduct and any excess phosphine. The method we now wish to describe utilizes polystyryldiphenylphosphine as a polymer-supported phosphine reagent.[12] The aromatic disulfide is dissolved in an aqueous THF solution containing a catalytic amount of HCl, followed by the addition of the insoluble phosphine reagent. A facile reductive cleavage of the disulfide ensues, followed by a workup consisting of a filtration to remove the resulting phosphine oxide (and any excess phosphine), a brief drying over $MgSO_4$, and removal of solvent under reduced pressure. In general the reactions are performed under a nitrogen atmosphere to prevent oxidation of the thiols formed, but deoxygenation of the solvent or other extraordinary measures are not required since a slight excess of phosphine reagent is used.

Various aromatic disulfides were investigated as outlined in Table I. The yields indicated in most cases are for isolated products without additional purification since such purification was frequently frustrated by air oxidation of the thiols. In all cases the isolated products were homogeneous by TLC, gave acceptable IR and NMR spectra, and were suitable for further conversions. The yields in virtually all cases were excellent with thiophenol, entry 1, being somewhat lower in yield due to its volatility and consequent loss during workup.

As evident from Table I, the reaction is quite tolerant of other functional groups although such groups did have a substantial effect upon reaction rates as evidenced by the minimum reaction conditions required to effect complete reductive cleavage of the disulfide as monitored by TLC. It should be noted that electron-withdrawing groups lead to a more rapid reaction, whereas the presence of electron-donating groups substantially reduces the reaction rate, i.e., entries 7, 8, and 9. This observation is in complete accord with the proposed mechanism since electron-deficient rings should lead to enhanced attack by the nucleophilic phosphorus and also to greater stability of the displaced thiolate anion. Entries 5 and 6 constitute an anomaly in this series since they required extended reflux times despite the presence of the electron-withdrawing carboxyl group. This reduced reactivity for ortho-substituted disulfides has been observed previously;[9] it may be magnified in this case by the steric bulk of the polystyrene backbone of the polymer-supported phosphine.

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**Table II. Alkylation of Thiol Intermediate**

| substd phenyl disulfide | alkylating agent | yield of [a] sulfide, % |
|---|---|---|
| 4-Cl | $CH_3I$ | 89 (13) |
| 4-Cl | $CH_3(CH_2)_3Br$ | 95 (14) |
| 3-$NO_2$ | $C_6H_5CH_2Cl$ | 90 (15) |

[a] All yields are based on products purified by preparative layer chromatography.

An attempt was made to extend the reaction to nonaromatic disulfides but without substantial success. Dibenzyl disulfide gave only a small amount of reductive cleavage despite a 30-h reflux. Apparently the triphenylphosphine is not sufficiently nucleophilic to induce reaction. The use of the more highly nucleophilic tri-*n*-butylphosphine has been reported to give efficient reductive cleavage of alkyl disulfides,[13] but we have not as yet prepared the corresponding polymer-supported alkylphosphine reagent.

Since some of the thiols prepared are quite sensitive to air oxidation, we felt it would be useful to explore the possibility of accomplishing a second reaction without isolation or purification of the aromatic thiol. In a series of three different reactions, the free thiol was found to undergo a rapid alkylation process. This two-step one-pot reaction consists of monitoring the disulfide cleavage until complete, followed by the addition of triethylamine and the alkylating agent. Table II lists the sulfide products prepared in this manner. In all cases the yields were excellent and preparative layer chromatography (PLC) afforded pure products with ease.

The use of water as the hydrogen source for the reductive cleavage reaction leads to the formation of 2 equiv of thiol. The use of carboxylic acids as the hydrogen source should yield a thiol ester as one product of the reaction. In accord with this proposal, 2,2′-dipyridyl disulfide (**10**) was found to react with benzoic acid in dry tetrahydrofuran solvent using the polymer-supported phosphine. Thiol ester **12**, formed in 78% yield, was easily separated from the 2-pyridinethione byproduct using PLC. These 2-pyridinethiol esters have been used extensively in the preparation of macrocyclic lactones,[14] and we are currently

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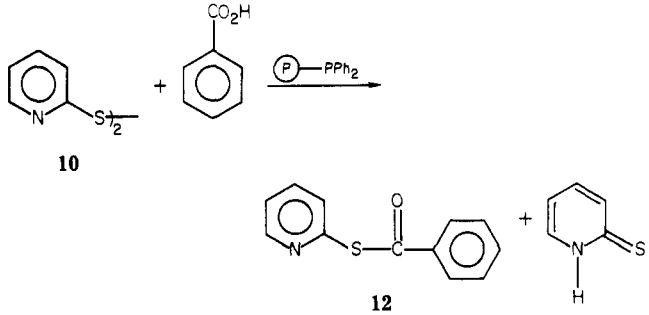

10 12

investigating the usefulness of the polymeric reagent in this regard.

In summary, the use of polystyryldiphenylphosphine represents a very effective procedure for the reductive cleavage of aromatic disulfides. The reaction offers high yields, mild reaction conditions, a wide tolerance of functional groups, and a convenient isolation procedure.

## Experimental Section

**General Procedures.** IR spectra were obtained on a Beckman Acculab instrument by using thin films on NaCl plates. NMR spectra were obtained on a Varian T-60 instrument with either $CCl_4$ or $CDCl_3$ as the solvent and with tetramethylsilane as an internal standard. Dry THF was obtained by distillation from sodium–benzophenone ketyl. Disulfides **1**, **3**, **4**, **5**, **8**, and **10** were obtained from commercial sources and were purified where necessary by recrystallization. Disulfides **2**, **7**, and **9** were prepared by oxidation of the corresponding thiols using $Me_2SO$ as an oxidant.[15] Disulfide **6** was prepared from **5** by a $H_2SO_4$-catalyzed esterification in refluxing methanol. The polystyrene beads (2% divinylbenzene, 200–400 mesh) were obtained from Eastman. All other reagents were used as received except for chlorodiphenylphosphine (Aldrich) that was vacuum distilled prior to use. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

**Preparation of Polystyryldiphenylphosphine.** Polystyrene beads were washed[12] and then brominated[16] to give a yellow solid with 4.59 mmol of Br/g of resin. The phosphine ligand was incorporated by the method described earlier[17] with the exception that the mixture was stirred 18 h at 25 °C following the addition of the lithium diphenylphosphide. After an additional 5 h of reflux, the reaction was quenched by the addition of 100 mL of 3:1 acetone–water. The polymer beads were collected by filtration and washed with the following sequence of solvents: 3:1 acetone–water, 2:3 $CH_2Cl_2$–$CH_3OH$, 3:1 $CH_2Cl_2$–$CH_3OH$, 9:1 $CH_2Cl_2$–$CH_3OH$, and finally $CH_2Cl_2$. Drying (0.1 torr, 90–100 °C, 24 h) gave a pale yellow solid with 2.79 mmol of P/g of resin.

**Typical Procedure for Disulfide Cleavage.** Bis(*p*-chlorophenyl)disulfide (287 mg, 1.00 mmol) was added to a 50-mL three-necked flask that had been thoroughly flushed with $N_2$. A solvent system consisting of 12 mL of THF and 1 mL of 0.1 N HCl was then added to dissolve the solid. Polystyryldiphenylphosphine (0.48 g, 1.34 mmol contained P) was then added, and the mixture was stirred at 25 °C. The reaction was monitored by TLC (silica gel, hexane solvent, UV visualization) and was found to be complete after 2 h. The polymer was removed by filtration and washed thoroughly with 40 mL of ether. The product was dried over $MgSO_4$, and removal of solvent gave 282 mg (98%) of a white solid, mp 49–51 °C (lit.[18] mp 52 °C).

All disulfides listed in Table I were reduced under these conditions except for the amino compound **8**. Prior to drying that product, a small amount of $NaHCO_3$ was added to neutralize the HCl and prevent loss of product as the hydrochloride salt. All products gave IR and NMR spectra compatible with the known structures with each showing clear evidence of the SH group.

**Typical Alkylation Procedure.** Bis(3-nitrophenyl)disulfide, 308 mg (1.00 mmol), was cleaved to the thiol in 15 min at 25 °C by using the reduction procedure above. Benzyl chloride (0.235 mL, 2.20 mmol) was then added, followed by 0.558 mL (4.00 mmol) of triethylamine. The solution immediately turned deep red and gradually faded to pale brown after 1.5 h. TLC revealed the complete consumption of thiol at that time. The polymer was removed by filtration and washed thoroughly with 50 mL of ether. The organic layer was washed with 2 × 10 mL of 1 M HCl, dried over $MgSO_4$, and concentrated by evaporation under reduced pressure. Purification by PLC (30% ether–hexane) afforded 444 mg (90%) of **15** as a pale yellow oil: $^1H$ NMR ($CDCl_3$) $\delta$ 7.40–8.25 (m, 4 H), 7.33 (s, 5 H), 4.18 (s, 2 H); IR (neat) 1530 (s), 1350 (s), 735 (s) $cm^{-1}$.

Anal. Calcd for $C_{13}H_{11}NSO_2$: C, 63.65; H, 4.52; S, 13.07; N, 5.71. Found: C, 63.61; H, 4.48; S, 13.19; N, 5.87.

Spectral and analytical data for the other alkylation products.

**13**: $^1H$ NMR ($CDCl_3$) $\delta$ 7.28 (s, 4 H), 2.43 (s, 3 H); IR (neat) 1470 (s), 1430 (s), 1095 (s), 1010 (s), 805 (s) $cm^{-1}$.

Anal. Calcd for $C_7H_7SCl$: C, 53.00; H, 4.45; S, 20.21; Cl, 22.35. Found: C, 53.09; H, 4.52; S, 20.06; Cl, 22.51.

**14**: $^1H$ NMR ($CDCl_3$) $\delta$ 7.27 (s, 4 H), 2.90 (t, $J$ = 7 Hz, 2 H), 1.30–1.80 (m, 4 H), 0.70–1.10 (m, 3 H); IR (neat) 1475 (s), 1395 (m), 1105 (s), 1020 (s), 820 (s) $cm^{-1}$.

Anal. Calcd for $C_{10}H_{13}SCl$: C, 59.84; H, 6.53; S, 15.97; Cl, 17.66. Found: C, 60.00; H, 6.51; S, 15.94; Cl, 17.68.

**Preparation of 12.** 2,2′-Dipyridyl disulfide (220 mg, 1 mmol) was dissolved in 12 mL of dry THF, followed by the addition of 134 mg (1.1 mmol) of benzoic acid and 0.56 g (1.56 mmol contained P) of polystyryldiphenylphosphine. The reaction was stirred 24 h at 25 °C at which time TLC revealed small amounts of the disulfide remaining. A 2-h reflux completed the reaction. The polymer was removed by filtration, followed by a thorough washing with 40 mL of ether. Removal of solvent and PLC purification (35% ethyl acetate–hexane) gave 167 mg (78%) of pale yellow oil: $^1H$ NMR ($CDCl_3$) $\delta$ 8.70–8.90 (m, 1 H), 8.10–8.35 (m, 2 H), 7.30–8.05 (m, 6 H); IR (neat) 1675 (s), 1575 (s), 1450 (s), 1420 (s), 1205 (s), 900 (s), 770 (s), 680 (s) $cm^{-1}$.

Anal. Calcd for $C_{12}H_9NSO$: C, 66.95; H, 4.21; S, 14.89; N, 6.51. Found: C, 67.05; H, 4.20; S, 14.68; N, 6.39.

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**Registry No.** **1**, 882-33-7; **2**, 1142-19-4; **3**, 3808-87-5; **4**, 537-91-7; **5**, 119-80-2; **6**, 5459-63-2; **7**, 5335-87-5; **8**, 722-27-0; **9**, 103-19-5; **10**, 2127-03-9; **12**, 10002-30-9; **13**, 123-09-1; **14**, 16155-34-3; **15**, 87740-10-1; PhSH, 108-98-5; *p*-$ClC_6H_4SH$, 106-54-7; 2,4,5-$Cl_3C_6H_2SH$, 3773-14-6; *m*-$NO_2C_6H_4SH$, 3814-18-4; *o*-$HSC_6H_4CO_2H$, 147-93-3; *o*-$HSC_6H_2CO_2CH_3$, 4892-02-8; *p*-$MeOC_6H_4SH$, 696-63-9; *p*-$H_2NC_6H_4SH$, 1193-02-8; *p*-$CH_3C_6H_4SH$, 106-45-6; $CH_3I$, 74-88-4; $CH_3(CH_2)_3Br$, 109-65-9; $PhCH_2Cl$, 100-44-7; $PhCO_2H$, 65-85-0; $LiPPh_2$, 4541-02-0; polystyrene, 9003-53-6; 2-pyridinethiol, 2637-34-5.

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