trogen is large, stabilization due to electron delocalization should still be substantial.

Experimental Section

General. NMR spectra were obtained with a Varian A60A spectrometer equipped with a variable temperature probe. $CDCl_3$ was used as solvent and $(CH_3)_4Si$ as internal standard. The temperature of each spectrum was determined from the separation between methyl and hydroxyl resonances of methanol. The standard methanol sample supplied by Varian was utilized. The temperature was determined both before and after each spectrum was obtained. The same methanol sample was used for all spectral measurements, which were consistently reproducible.

Preparation of 2,2-Dibenzyl-1,1,3,3-tetramethylguanidine Chlorides (5a–d). In 150 mL of benzene was dissolved 0.1 mol of benzyl chloride ($ArCH_2X$). (The source of benzyl chlorides was Aldrich Chemical Co.) To this solution was added 0.1 mol of TMG, and the flask was stoppered and allowed to stand at room temperature for approximately 24 h. The crystalline precipitate (P_1) was filtered off and the filtrate evaporated down to approximately 10 mL on a rotary evaporator. The crystalline solid (P_2) formed on evaporation was filtered from the remaining liquid and washed with a small quantity of cold benzene. Both P_1 and P_2 were then subjected to fractional recrystallization from *o*-dichlorobenzene. The products P_1 and P_2 were combined and recrystallized from *o*-dichlorobenzene. This final product was then vacuum-dried with warming for 24 h.

Preparation of 2-Benzyl-1,1,3,3-tetramethylguanidine Chloride (2a). In 100 mL of benzene was dissolved 0.2 mol of TMG. To this was added slowly a solution of 0.1 mol of benzyl chloride in 50 mL of benzene, and the flask was stoppered and allowed to stand for 24 h. The separation procedure was as described above.

Satisfactory analytical data (±0.2% for C, H, and N) were reported for all compounds (Ed.).

Registry No.—**2a,** 68051-05-8; **5a,** 68081-52-7; **5b,** 68081-53-8; **5c,** 68081-54-9; **5d,** 68081-55-0; benzyl chloride, 25168-05-2; TMG, 80-70-6.

References and Notes

(1) H. Kessler and D. Leibfritz, *Tetrahedron*, **25,** 5127 (1969).
(2) H. Kessler and D. Leibfritz, *Tetrahedron*, **26,** 1805 (1970).
(3) H. Kessler, *Tetrahedron Lett.*, 2041 (1968).
(4) V. J. Baver, W. Fulmor, G. O. Norton, and S. R. Safir, *J. Am. Chem. Soc.*, **90,** 6846 (1968).
(5) H. Kessler and D. Leibfritz, *Tetrahedron Lett.*, 427 (1969).
(6) H. Kessler and D. Leibfritz, *Chem. Ber.*, **104,** 2158 (1971).
(7) (a) I. O. Sutherland, *Annu. Rep. NMR Spectrosc.*, **4,** 83–91 (1971), and references therein; (b) K. C. Ramey, D. C. Lini, and G. Krow, *Ibid.*, **6A,** 160–164 (1975).
(8) T. Bally, P. Diehl, E. Haselbach, and A. S. Tracey, *Helv. Chim. Acta*, **58,** Fasc. 8, 2398 (1975).
(9) The authors were comparing their results with Kessler's determinations, which were made at coalescence temperatures of approximately 300 K. For example, $\Delta G^{\ddagger}$ is 12.9 kcal/mol (T_c = 238 K) for 2-phenyl-1,1,3,3-tetramethylguanidine salt. See ref 1.
(10) J. F. Capitani and L. Pederson [*Chem. Phys. Lett.*, **54,** 547 (1978)] report 14.97 kcal/mol.
(11) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, 1962, p 134.
(12) A. V. Santoro, unpublished results.

Reaction of *p*-Quinones with Thioamides

V. Horak* and W. B. Manning

Department of Chemistry, Georgetown University, Washington, D.C. 20057

Received June 6, 1978

Reaction of thioacetamide with 1,4-benzoquinone produced 3a-hydroxy-2-methyl-1,3-benzothiazol-6(3a*H*)-one (**1**), mercaptohydroquinone (**3**), and its disulfide **4** as the main sulfur-containing products. The yield of **1**, **3**, and **4** varied depending on reactant ratio and solvent. The chemistry of **1** as well as of its precursor, iminothioacetylhydroquinone (**8**), is characterized by the tendency to eliminate acetonitrile. This was found in three separate reactions as well as in the fragmentation observed by mass spectrometry. Methyl-1,4-benzoquinone behaved similarly to 1,4-benzoquinone and thiobenzamide similarly to thioacetamide. 2,5-Di-*tert*-butyl-1,4-benzoquinone and 2-methyl-1,4-naphthoquinone with thioacetamide produced S_8 and the respective hydroquinone. A new nonoxidative disulfide formation (from compound **1** and a thiol **3**) is described.

Reactions of bidentate nucleophiles with *p*-quinones represent common synthetic routes to many heterocycles, either nonaromatic, as exemplified by reactions of β-amino alcohols[1] or cysteine,[2] or aromatic, represented by Nenitzescu synthesis of 5-hydroxyindoles.[3] Many of the above reactions involve oxidation of the primary product with a second quinone molecule. The formation of a substituted quinone enables the cyclization step.

In this paper the results of reactions of *p*-quinones with bidentate thioamides and the chemistry of the respective products are reported. In the past certain compounds with thioamide structure yielded only Michael addition products with *p*-benzoquinone,[4] whereas others such as thiourea produced a benzothiazole derivative.[5a] In all of the examples shown above, the primary nucleophilic attack resulted from the sulfur atom. However, no reaction of *p*-quinones with simple thioamides has been documented in the literature. In the studies reported in this paper, reaction of 1,4-benzoquinone with thioacetamide was examined in some detail. The studies were further extended to other quinones (methyl-1,4-benzoquinone, 2,5-di-*tert*-butyl-1,4-benzoquinone, and 2-methyl-1,4-naphthoquinone) and to another simple thioamide (thiobenzamide).

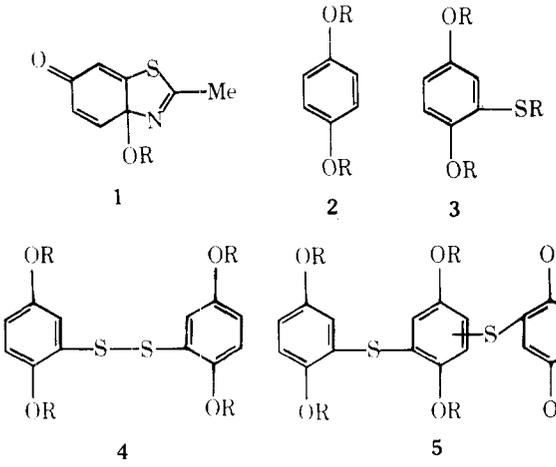
Discussion

Reactions between thioamides and 1,4-benzoquinone showed rapid darkening in early stages of the process and produced generally variable quantities of tarry products. This made determination of the mass balance of the reaction virtually impossible. The reaction of thioacetamide with 1,4-benzoquinone was examined using different solvents and varying the ratio of reactants from 1:1 to 1:2. The results of the reaction were evaluated in either preparative fashion or by gas chromatographic analysis after acetylation using authentic samples as standards (Table I). Small differences were observed when the results from preparative and analytical types of experiments were compared. The following compounds were identified as the reaction products: 3a-hydroxy-2-methyl-1,3-benzothiazol-6(3a*H*)-one (**1**), hydroquinone (**2**), mercaptohydroquinone (**3**), dithiobis[hydroquinone] (**4**), 2,6-(or 2,5-)bis(2,5-dihydroxyphenylmercapto)hydroquinone (**5**), and their acetyl derivatives. The structure of compound

0022-3263/79/1944-0120$01.00/0

Table I. Quantitative GC Analyses of Acetylated 9, 10, 11, and 12 of the 1,4-Benzoquinone (14)–Thioacetamide (15) Reaction

	reactants, mg (mmol)		products, mg (mmol, % yield)			
solvent	14	15	9	10	11	12
(1) ethanol	50 (0.46)	17 (0.23)	19.5 (0.20, 40)	39.5	<0.1	<0.1
(2) ethanol	50 (0.46)	34 (0.46)	<0.1	42.0 (0.22, 44)	10.0 (0.038, 8)	14.0 (0.033, 13)
(3) dioxane	50 (0.46)	17 (0.23)	0.13 (0.01, 3)	22.0 (0.11, 22)	9.0 (0.034, 7)	6.8 (0.015, 6)
(4) dioxane	50 (0.46)	34 (0.46)	<0.1 (0.13, 26)	26.0 (0.13, 26)	9.0 (0.034, 7)	6.5 (0.014, 6)

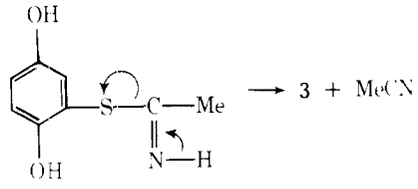


1 2 3 4 5

R = H, Ac

1 was determined by corroborating spectroscopic data with qualitative microchemical tests[5b] and results of chemical reactions involving Raney nickel desulfurization (produced hydroquinone 2). Compounds 1 and 2 are products which result from the sequence of steps shown in Scheme I. With a 2:1 ratio of reactants (6 and 7), the yield of 1 was 23% in a preparative experiment and 35% in a GC-monitored experiment; the yields of 2 were 38 and 40%, respectively. The formation of 2 in quantities greater than stoichiometrically required to form 1 (see Scheme I) can be explained by the formation of S_8 and the disulfide 4 via oxidative processes involving 1,4-benzoquinone (6).

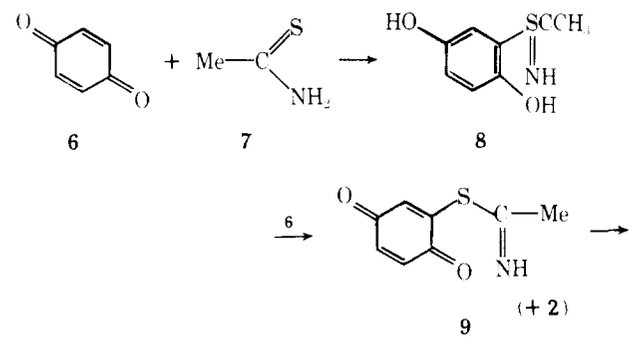
Formation of 3 is explained by elimination of acetonitrile from 8 rather than by its hydrolysis. Whereas no acetamide



8

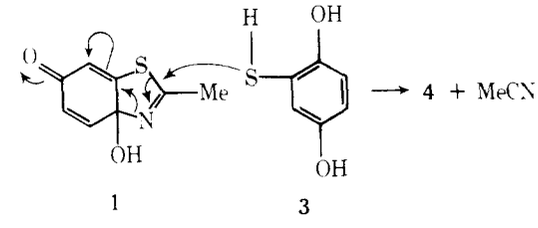
could be detected among the reaction products of 1,4-benzoquinone and thioacetamide, acetonitrile was determined by GC in an experiment conducted using dioxane as solvent. It accounted for 46% of the total thioacetamide used. This type of elimination has been documented earlier in reactions of thioacetamide with Mannich bases[6] and propiolamidine-type structures.[7] The absence of 3 and 4 in a GC-monitored experiment with a 2:1 ratio of reactants (6 and 7) in ethanol indicates that the oxidation of 8 to 9 and its cyclization to 1 are faster under the experimental conditions than the elimination of acetonitrile. However, in the experiment with equimolar reactants, no cyclic compound 1 could be determined among the reaction products and the main sulfur-containing products

Scheme I



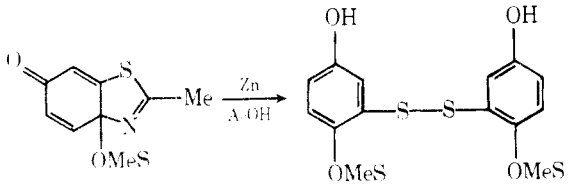
6 7 8 9 (+ 2) 1

found were thiol 3 and the disulfide 4. It is evident that thiol 3 is a source for disulfide 4, but in systems deficient in oxidizing reagents (e.g., quinone) it cannot be produced by an oxidative pathway. Thus, in an independent experiment approximately equimolar quantities of 1 and 3 produced disulfide 4 rapidly and almost quantitatively, possibly via the reaction step



1 3

The fast rate of this elimination reaction also explains why even traces of the cyclic product 1 could not be found in an experiment in which equimolar amounts of reactants 6 and 7 were used in ethanol. Because the oxidation of the Michael adduct 8 (followed by cyclization) is faster than elimination of acetonitrile, some of the cyclized product 1 should be formed at early stages of the reaction when quinone is still on hand for the oxidation process. However, in later stages the Michael adduct 8 in absence of quinone undergoes elimination, and the thiol 3 formed consumes all cyclized product 1 in a process shown above. Furthermore, the same reaction is used to explain the formation of the disulfide 4 from the cyclic compound 1 in reductive processes. Whereas sodium borohydride is ineffective, sodium dithionate, zinc and acetic acid, aluminum isopropoxide in isopropyl alcohol, and diborane all produce 4 in medium to good yields. It is assumed that the thiol 3 necessary to produce 4 from the unreacted 1 is formed via a reductive elimination step. No reduction of disulfide 4 to the thiol 3 under any of the experimental conditions used could be observed. Substitution of hydroxyl in cyclic compound 1 with the better leaving group *O*-mesyl (compound 10) did not change the outcome of the reduction observed with unsubstituted 1; the product 11 was the partially mesylated

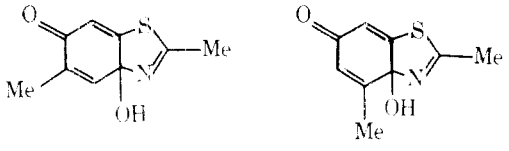


10 11

disulfide **4**. Compound **11** was identified by spectra and by exhaustive mesylation to produce a tetramesylated **4**.

The reaction between 1,4-benzoquinone (**6**) and thioacetamide (**7**) (2:1 ratio) was found to be strongly solvent dependent. Ethanol and dioxane were observed to affect primarily the distribution of products **1**, **3**, and **4**, whereas acetic acid altered the reaction qualitatively. Compared to the reaction in ethanol, dioxane formed cyclic product **1** in much lower yield (3% vs. 25%) and afforded thiol **3** and disulfide **4** as the principal sulfur-containing products. The failure to form much of compound **1** in dioxane in an excess of quinone suggested a change in the rates of the two competitive reactions involving the Michael adduct **8**. Thus, in ethanol the oxidation (and ring closure: **8** → **9** → **1**) was promoted, whereas elimination (**8** → **3** + MeCN) predominated in dioxane. In acetic acid the pathway **8** → **9** → **1** was not observed at all (absence of **1** and **4**), and the absence of acetoamide suggests that the needed thiol **3** for the formation of **5** results from the elimination step.

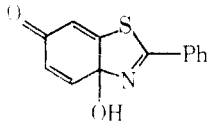
Examination of other quinones for their reactivities toward thioacetamide produced variable results. Thus, an excess of methyl-1,4-benzoquinone in ethanol yielded a mixture of isomeric products in about equal amounts (**12** and **13**) with



12 13

structures analogous to that of **1**. On the contrary, 2,5-di-*tert*-butyl-1,4-benzoquinone and 2-methyl-1,4-naphthoquinone did not react with thioacetamide in ethanol during short reaction times. Prolonged refluxing results in the formation of S_8 and the respective hydroquinones. Thus, the substituents hindered the addition of this nucleophile and the quinones acted as oxidizing agents, producing elemental sulfur from thioacetamide.

Thiobenzamide, with an excess of 1,4-benzoquinone in ethanol, produced compound **14** in 51% yield.



14

The results of the study of reactions between simple thioamides and *p*-quinones are summarized as follows. (i) Thioamides in ethanol react with an excess of sterically unhindered quinones to form cyclic products typically represented by 3a-hydroxy-2-methyl-1,3-benzothiazol-6(3a*H*)-one (**1**). Other quinones act as oxidizers only. (ii) Reduction products of **1** and its *O*-mesyl derivative undergo another reaction (by elimination of acetonitrile), rather than aromatization, to the 2-substituted 6-hydroxybenzothiazoles. (iii) The dominant property governing the chemistry of products formed from thioamide and 1,4-benzoquinone is elimination of acetonitrile. This tendency was observed in three different reactions, i.e., decomposition of **8**, reduction of **1**, and reaction of **1** with **3**. The same tendency was shown in mass spectrometric fragmentation of compounds **1**, **12**, **13**, and **14** (elimination of benzonitrile). (iv) In an unprecedented reaction, thiol **3** and cyclic compound **1** produced a disulfide **4**.

Experimental Section

The following instruments were used for spectroscopic measurements: Perkin-Elmer Model 457 and 700 IR spectrophotometers, Varian Model A-60 and A-60-A NMR spectrometers, LKB 900 mass spectrometer (courtesy of Mr. William Comstock, NIH, Bethesda), Finnigan 3300 mass spectrometer equipped with an MS 6000 data system, AEI MS-1201 mass spectrometer, and a Cary 14 UV–vis spectrophotometer. A Varian Model 1400 with an FI detector was used for GC analysis with SE-30 (5.7%) on Chromosorb W (100–120 mesh) or QF-1 (4%) on Chromosorb W (100–120 mesh) columns (6 ft long, 2 mm i.d.) and a Hewlett-Packard HP 3370B automatic integrator (1% error). For GC analysis, 2.0-μL samples (3% error) were injected.

The following chemicals were used: thioacetamide was an ACS grade (mp 112–114 °C) J. T. Baker Co. product, *p*-benzoquinone (98%; mp 113–115 °C; used freshly sublimed) was an Aldrich Co. product, acetic anhydride was an ACS grade J. T. Baker Co. product, and methanesulfonyl chloride (98%) was an Aldrich Co. product. Bakerflex silica gel IB-F was used in TLC chromatography, and a 254-nm UV source was used for spot detection. J. T. Baker "For Chromatography" (60–200 mesh) silica gel was used for column chromatography, and fractions collected automatically were monitored with TLC.

Reaction of 1,4-Benzoquinone with Thioacetamide in Ethanol. A solution of 1,4-benzoquinone (8.8 g, 81 mmol) and thioacetamide (3.1 g, 41 mmol) in 500 mL of ethanol was kept for 10 min at 65 °C. Then the volume was reduced to 15–20 mL at water aspirator vacuum, the mixture was filtered, and the filtrate was chromatographed on 280 g of silica gel with a chloroform–ethyl acetate (4:1) mixture. From fractions (monitored with TLC) using a carbon tetrachloride–ethyl acetate (3:1) mixture was recovered 0.1 g (8%) of elemental sulfur (mp 117–119 °C), 2.0 g (27.5%) of crude 3a-hydroxy-2-methyl-1,3-benzothiazol-6(3a*H*)-one (**1**; mp 151–155 °C), and 3.4 g (38%) of hydroquinone (**2**). From the tarry product eluted from the column with chloroform–ethyl acetate (2:1), 0.4 g (7%) of dithiobis[hydroquinone] tetracetate (**4**) was obtained after acetylation with acetic anhydride and sodium acetate.

Product **1** was purified by crystallization from dilute methanol to yield 1.6 g (22%) of pure white crystals of mp 154–155 °C with the following spectroscopic data: MS *m/e* (relative intensity) 181 (M^+, 37), 140 (17), 112 (100), 111 (12); UV (methanol) λ_{max} (ε) 226 (11 900), 245 (14 900), 317 (4300) nm; IR (KBr pellet) 3150 (OH), 1649 (CO), 1372 (CH_3), 1183 cm^{-1}; NMR (dioxane-d_8) δ 7.7 (1 H, broad s, OH), 6.7–6.2 (3 H, olefinic H), 1.98 (3 H, s, CH_3). Anal. Calcd for $C_8H_7NO_2S$: C, 53.04; H, 3.96; N, 7.73; S, 17.67. Found: C, 53.07; H, 3.64; N, 7.62; S, 17.91.

Hydroquinone (**2**) was identified by its NMR, IR, and UV spectra using an authentic sample. The tetraacetate **4** was compared with an authentic sample prepared by acetylation of **4** (R = H)[8] and showed the following data: IR (CCl_4) 1770 (CO), 1470, 1375 (CH_3), 1210, 1170 cm^{-1}; NMR (CCl_4) δ 7.5–7.2 (2 × 3 H, aromatic), 2.42 (2 × 3 H, s, acetyl), 2.38 (2 × 3 H, s, acetyl); MS *m/e* (relative intensity) 450 (M^+, 31), 408 (39), 366 (15), 324 (14), 282 (8), 226 (15), 184 (100), 142 (40).

Reaction of 1,4-Benzoquinone with Thioacetamide in Dioxane. *p*-Benzoquinone (1.1 g, 10 mmol) and thioacetamide (375 mg, 5 mmol) were heated in 40 mL of dioxane at 65 °C for 10 min. The solvent was evaporated in vacuum to dryness, and the ethyl acetate extract was chromatographed on 50 g of silica gel (chloroform–ethyl acetate, 4:1) to yield 35 mg (22%) of sulfur (mp 116–119 °C), 15 mg (2%) of compound **1** (mp 150–155 °C), 260 mg (24%) of hydroquinone (mp 168–170 °C), and 90 mg of an oil. The latter, after acetylation (5 mL of acetic anhydride and 0.5 g of sodium acetate), produced 110 mg of a solid. Preparative TLC of the acetylation product (55 mg) yielded, on two silica gel plates (10 × 20 cm, 1.5 mm thick, chloroform), 22 mg (2%) of mercaptohydroquinone triacetate (**3**; oil) and 29 mg (3%) of dithiobis[hydroquinone] tetraacetate (**4**; mp 133–135 °C), both identified by IR, NMR, and MS data using authentic samples as standards.

Reaction of 1,4-Benzoquinone with Thioacetamide in Acetic Acid. Reaction of 1.7 g (22.6 mmol) of thioacetamide and 4.5 g (41.6 mmol) of 1,4-benzoquinone in 80 mL of acetic acid at room temperature produced, after 1 h, a complicated mixture of products (TLC on silica gel plate; chloroform–ethyl acetate, 1:1) in which none of the compound **1** could be detected. A 20-mL amount (about one-fourth

of the total volume) of the mixture was evaporated under vacuum. Water (50 mL) was added to the resulting dark oil. After the remaining acetic acid was neutralized with potassium carbonate, the organic products were extracted with ethyl acetate. Chromatography of the extract on 120 g of silica gel (chloroform–ethyl acetate, 5:1) gave 290 mg (26%) of hydroquinone and 185 mg (25%) of 2,6-(or 2,5-)bis(2,5-dihydroxyphenylmercapto)hydroquinone (**5**; oil), identified as the hexaacetate: mp 208–210 °C; IR (KBr pellet) 1770 (CO), 1490, 1372 (CH_3), 1215 (CO), 1180 (CO), 1170, 1021 cm^{-1}; NMR ($CDCl_3$) δ 7.5–7.2 (8 H, aromatic), 2.5–2.4 (6 × 3 H, acetyl); MS *m/e* (relative intensity) 642 (M^+, 27), 600 (44), 558 (93), 516 (100), 474 (90), 432 (45), 390 (18), 292 (16), 280 (6), 279 (14), 248 (71), 143 (20), 142 (15). Anal. Calcd for $C_{30}H_{26}S_2O_{12}$: C, 56.07; H, 4.05; S, 9.97. Found: C, 55.95; H, 4.20.

GC-Monitored Reactions of 1,4-Benzoquinone and Thioacetamide in Ethanol and Dioxane. Both reactants (quantities are given in Table I) and 5 mL of the respective solvent were kept at 70 °C for 5 min. After the solvent was removed under vacuum, the remaining mixture of products was acetylated with 10 mL of acetic anhydride and 1 g of sodium acetate at 70 °C for 15–20 min. A 2.0-μL amount of this solution was injected onto and separated on an SE-30 column (temperature programmed from 150–240 °C using a 6 °C/min regime, injection port 230–245 °C, detector 265–275 °C, 40 mL/min He flow rate). The retention times of acetylated **1**, **2**, **3**, and **4** authentic samples were 6.74, 12.75, 14.40, and 14.98 min, respectively. For calibration purposes, 2.0-μL amounts of solutions of authentic samples of acetylated compounds **1**, **2**, **3**, and **4** of known concentration were chromatographed and the peaks integrated. The results of experiments in which 2:1 and 1:1 reactant ratios of 1,4-benzoquinone–thioacetamide were used and the solvents (ethanol and dioxane) varied are reported in Table I.

In order to detect and quantify acetonitrile, the reaction mixture from 1.0 g (9.3 mmol) of 1,4-benzoquinone, 360 mg (4.8 mmol) of thioacetamide, and 10 mL of dioxane was distilled, 7 mL was collected, and 2.0 μL of the distillate was chromatographed using a QF-1 column (80 °C isothermal, 40 mL/min He flow rate). Acetonitrile was identified as the peak with a retention time of 0.92 min using an authentic sample as a standard and mass spectroscopy. Integration of the peak accounted for amounts of acetonitrile corresponding to 46% of the thioacetamide used in the experiment.

Reaction of Methyl-1,4-benzoquinone[12] and Thioacetamide. Methyl-1,4-benzoquinone (500 mg, 4.1 mmol; prepared according to ref 11; mp 66–67 °C), thioacetamide (150 mg, 2.0 mmol), and 40 mL of ethanol were heated at 60–65 °C for 80 min. Workup similar to that with 1,4-benzoquinone yielded 85 mg (22%, mp 110–114 °C) of a mixture of 2,4- and 2,5-dimethyl-3a-hydroxy-1,3-benzothiazol-6(3a*H*)-one (**12** and **13**) as the main sulfur-containing product besides 15 mg (4%, mp 116–117 °C) of one of the two isomers. The latter showed the following characteristics: IR (KBr pellet) 3200 (OH), 1649 (CO), 1375 (CH_3), 1185 cm^{-1}; MS *m/e* (relative intensity) 195 (M^+, 46), 154 (20), 126 (100), 97 (18), 85 (13); NMR ($CDCl_3$) δ 6.58 (1 H, s, –CH=CR–), 6.43 (1 H, q, –CH=C(CH_3)–), 2.15 (3 H, s, CH_3), 2.09 (3 H, d, J = 3 Hz, –CH=C(CH_3)–), 2.02 (1 H, s, OH). Anal. Calcd for $C_9H_9NO_2S$: C, 55.38; H, 4.61; N, 7.18; S, 16.41. Found: C, 55.42; H, 4.72; N, 7.01.

The mixture showed the following data: (IR and MS were fully identical with the above data) NMR ($CDCl_3$) δ 6.56 (1 H, s), 6.41 (1 H, q), 6.25 (1 H, s), 6.16 (1 H, q), 2.14 (6 H, s), 2.1 (6 H, m), 2.0 (1 H, m). Anal. Calcd for $C_9H_9NO_2S$: C, 55.38; H, 4.61; N, 7.18; S, 16.41. Found: C, 55.37; H, 4.80; N, 7.09.

Reaction of 1,4-Benzoquinone with Thiobenzamide. Thiobenzamide (135 mg, 1 mmol; mp 116–117 °C; prepared according to ref 9) and 1,4-benzoquinone (215 mg, 2.0 mmol) were refluxed in 10 mL of ethanol for 20 min. Benzonitrile was detected in the reaction mixture by its odor. After evaporating to dryness, the remaining material was chromatographed on 25 g of silica gel. Elution with chloroform produced traces of sulfur (mp 116–118 °C) and 120 mg (51%) of 3a-hydroxy-2-phenyl-1,3-benzothiazol-6(3a*H*)-one [14] as a yellow solid: mp 126–128 °C; IR (KBr pellet) 3350 (OH), 1645 (CO), 1590, 1440, 1430 and 1190 (CO) cm^{-1}; NMR ($CDCl_3$) δ 8.0 (2 H, aromatic), 7.6 (1 H, s, OH), 7.5 (3 H, aromatic), 6.7–6.5 (3 H, olefinic); MS *m/e* (relative intensity) 243 (M^+, 24), 140 (30), 112 (100), 104 (21), 103 (14). Anal. Calcd for $C_{13}H_9NO_2S$: C, 64.19; H, 3.70; N, 5.76; S, 13.17. Found: C, 64.06; H, 3.55; N, 5.66; S, 13.13.

Reaction of 3a-Hydroxy-2-methyl-1,3-benzothiazol-6(3a*H*)-one (1) with Mercaptohydroquinone (3). A solution of compounds **1** (200 mg, 1.1 mmol) and **3** (140 mg, 1.0 mmol; prepared according to ref 10) in 5 mL of ethanol immediately after mixing showed complete absence of compound **3** (TLC on silica gel; chloroform–ethyl acetate, 3:1). The solid recovered from the reaction mixture after column chromatography produced (25 g of silica gel; chloroform–ethyl acetate, 4:1) 15 mg (7.5%) of unreacted compound **1** and 265 mg (93%) of dithiobis[hydroquinone] (**4**; oil). Acetylation of the latter compound yielded tetraacetate (mp 133–235 °C) with IR and NMR spectra identical with those of an authentic sample.

Zinc Reduction of 3a-Hydroxy-2-methyl-1,3-benzothiazol-6(3a*H*)-one (1). Compound **1** (80 mg, 1.5 mmol) in 5 mol of acetic acid was stirred with zinc powder (100 mg, 1.5 mmol) at room temperature until all of the starting material was consumed (TLC on silica gel; chloroform–ethyl acetate, 3:1). Filtration, evaporation, and column chromatography on 10 g of silica gel (chloroform–ethyl acetate, 3:1) yielded 65 mg (81%) of dithiobis[hydroquinone] (**4**), which after acetylation yielded product of mp 135–136 °C.

Preparation of 3a-*O*-Methanesulfonyl-2-methyl-1,3-benzothiazol-6(3a*H*)-one (10). To a solution of compound **1** (90 mg, 0.5 mmol) and triethylamine (200 mg, 1.5 mmol) in 12 mL of methylene chloride was added gradually redistilled methanesulfonyl chloride while the progress of the reaction was monitored with TLC (silica gel plate; chloroform–ethyl acetate, 5:1). After 50 μL of the reagent was added (reaction time 25 min), the reaction mixture was evaporated and chromatographed on two 20 × 20 cm silica gel plates (2 mm thick, chloroform). Compound **10** (98 mg, 77%, mp 48–51 °C) was recovered from the zone of R_f 0.3: IR (KBr pellet) 1655 (CO), 1470, 1185 (SO_2), 1152 (SO_2) cm^{-1}; MS *m/e* (relative intensity) 259 (M^+, 48), 218 (21), 196 (36), 139 (100), 111 (65).

Reduction of 3a-*O*-Methanesulfonyl-2-methyl-1,3-benzothiazol-6(3a*H*)-one (10). To a solution of compound **10** (80 mg, 0.31 mmol) in 5 mL of glacial acetic acid was added purified zinc powder (50 mg, 0.75 mmol; see ref 13), and the mixture was stirred at room temperature for 15 min. After filtration, evaporation of the solvent under vacuum, and chromatography on two TLC silica gel plates (20 × 20 cm, 2 mm thick; chloroform–ethyl acetate, 5:1), 45 mg (33%) of white solid was isolated, mp 118–121 °C, the spectra of which were consistent with the structure of dithiobis[hydroquinone] dimesylate (**11**): IR (KBr) 3280 (OH), 1390, 1180 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 7.5–7.0 (2 × 3 H, aromatic), 3.22 (2 × 1 H, OH), 3.15 (2 × 3 H, SO_2CH_3); MS *m/e* (relative intensity) 438 (M^+, 16), 359 (4), 219 (38), 141 (100), 79 (81).

Exhaustive mesylation of **11** using the method described in a previous experiment yielded dithiobis[hydroquinone] tetramesylate (oil): MS *m/e* (relative intensity) 594 (M^+, 15), 516 (88), 470 (55), 438 (100).

Registry No.—**1** (R = H), 68001-47-8; **2** (R = H), 123-31-9; **3** (R = Ac), 68001-48-9; **3** (R = H), 2889-61-4; **4** (R = Ac), 68081-49-0; **5** (R = H), 68001-76-3; **10**, 68001-50-3; **11**, 68001-51-4; **12**, 68001-52-5; **13**, 68001-53-6; **14**, 68001-54-7; 1,4-benzoquinone, 106-51-4; thioacetamide, 62-55-5; methyl-1,4-benzoquinone, 553-97-9; thiobenzamide, 2227-79-4; thiobis[hydroquinone] tetramesylate, 68001-55-8.

References and Notes

(1) K. D. Murtrey and G. D. Daves, Jr., *J. Org. Chem.*, **35**, 4252 (1970).
(2) R. Kuhn and H. Beinert, *Ber.*, **77**, 606 (1944).
(3) C. D. Nenitzescu, *Bull. Soc. Chim. Romania*, **11**, 37 (1929); *Chem. Abstr.*, **24**, 110 (1930).
(4) A. Pollak, B. Stanovik, and M. Tisler, *Monatsh. Chem.*, **97**, 1523 (1966).
(5) (a) P. T. S. Lau and T. E. Gompf, *J. Org. Chem.*, **35**, 4103 (1970); (b) F. Feigl, V. Gentil, and E. Jungreis, *Michrochim. Acta*, 47 (1957).
(6) N. S. Gill, K. B. James, and K. T. Potts, *J. Am. Chem. Soc.*, **74**, 4923 (1952).
(7) H. Fugita, R. Endo, and K. Murayama, *Bull. Chem. Soc. Jpn.*, **45**, 1582 (1972).
(8) G. Jacini, *Gazz. Chim. Ital.*, **77**, 252 (1947).
(9) J. V. Burakevich and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 51 (1965).
(10) W. Alcalay, *Helv. Chim. Acta*, **36**, 578 (1947).
(11) E. B. Vliet, "Organic Syntheses", Collect. Vol. 1, Wiley, New York, 1953, p 482.
(12) J. Cason, *Org. React.*, **4**, 305 (1948).
(13) L. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, 1967, p 1276.
(14) R. K. Crossland and K. L. Servic, *J. Org. Chem.*, **35**, 3195 (1970).