1,4-Addition of Triazolium Thiolates to Quinones

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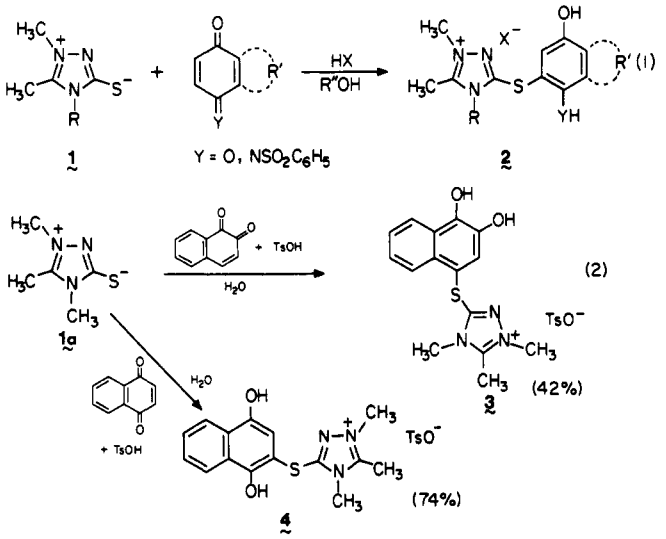
In the presence of a protic acid, 1,2,4-triazolium-3-thiolates **1** undergo 1,4-Michael additions to quinones to form the corresponding thioether-substituted hydroquinone salts **2**. When, however, tetrafluoroboric acid is added to a stirred aqueous suspension of triazolium thiolate **1a** and *p*-benzoquinone, the 2,5-bis(triazolium thiolate) adduct **6**, rather than the expected monoadduct **5**, is isolated. Since *o*-quinones are extremely reactive and often difficult to isolate, they can be generated in situ by oxidation of the corresponding catechols with hydrogen peroxide in the presence of a protic acid and then trapped by a triazolium thiolate to form thioether hydroquinone salts **8**. Triazolium thiolate **1a** adds to a 1,4-naphthoquinone imine to give the (triazoliothio)-4-(benzenesulfonamido)-1-naphthol salt **11**. Triazoliothioquinone tetrafluoroborates **16**, which can be isolated as crystalline yellow salts, are rapidly formed by oxidation of the corresponding hydroquinone salts **2** with nitrosonium tetrafluoroborate in acetonitrile.

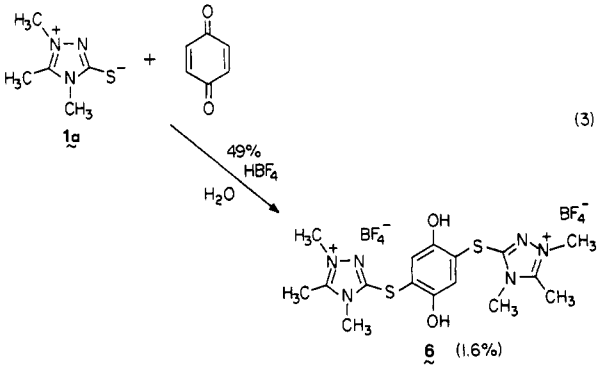
In 1964, two papers from these laboratories described the 1,4-addition of 1-phenyl-2-tetrazoline-5-thione (HPMT) to 1,4-quinones.[1] The proton of HPMT is acidic enough so that this ionic 1,4-addition to various quinones proceeds without an added proton source such as a mineral acid. Mesoionic mercaptans, such as the triazolium thiolates **1**,[2] however, do not have ionizable (acidic) protons and fail to react with quinones. When an external proton source is present, however, the triazolium thiolates **1** add to various quinones (and to a quinone imine) to form the (triazoliothio)hydroquinone (or hydroquinone imine) salts **2** (reaction 1). These observations provide the first documented examples of acid-catalyzed 1,4-additions of azolium thiolates to quinones.



Tables I and II summarize a few of these ionic additions of 1,4,5-trimethyl-1,2,4-triazolium-3-thiolate **1a** (R = CH_3) (Table I) and of other azolium thiolates (Table II) to 1,4-benzoquinones. In the presence of *p*-toluenesulfonic acid, triazolium thiolate **1a** also undergoes a Michael addition to 1,2- or 1,4-naphthoquinone to give the corresponding naphthohydroquinone adducts **3** and **4**, respectively (reaction 2).

Generally, the protic acid (1.5 equiv) is added to an aqueous, methanolic, or 50% aqueous methanolic suspension of the quinone (1.0 equiv) and triazolium thiolate (1.1 equiv), and the mixture is mechanically stirred at ambient temperature in a nitrogen atmosphere for 18 h. Since the yellow quinone color usually disappears rapidly, the 1,4-Michael addition is a facile process at room temperature. If the salt has not separated at the end of 18 h, the reaction medium is evaporated to dryness, and the salts are generally purified by suspension in or crystallization from ethanol, aqueous ethanol, or methanol/ethyl ether. Water, methanol, or mixtures of both can be used as the protic solvent for these Michael additions; the choice of solvent depends on which one best dissolves *both* reactants.

When tetrafluoroboric acid was added to a stirred aqueous suspension of triazolium thiolate **1a** and *p*-benzoquinone, the bis(triazolium thiolate) adduct **6** rather than the expected mono adduct **5** separated from solution in 1.6% yield (reaction 3). The rate of triazolium thiolate



addition to *p*-benzoquinone was slow enough so that reversible cross oxidation by unreacted *p*-benzoquinone of the initially formed **5** gave **7**.[3] Benzoquinone **7** then reacted with an equivalent of triazolium thiolate **1a** to give the bis adduct **6** (reaction 4). No attempt was made, however, to analyze the filtrate for additional **6** or for salt **5**. The symmetry of **6** was deduced from its ^1H NMR spectrum. A sharp singlet at δ 6.92 was assigned to the two para aromatic protons. Three singlets, each of which corresponds to six protons, were assigned to the three different methyl groups on the two triazoliothio moieties.

When *p*-benzoquinone was added slowly to a stirred aqueous solution of triazolium thiolate **1a** and tetrafluoroboric acid, the mono adduct **5** separated from solution in 71% yield. *p*-Benzoquinone was probably never present in large enough quantity to oxidize appreciable amounts of **5** to **7**.

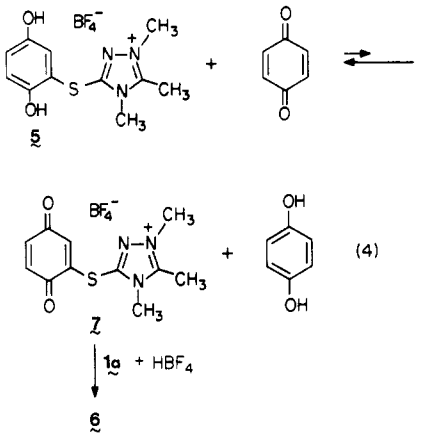
Although *o*-quinones can be difficult to isolate, they can be generated in situ and trapped by sulfur nucleophiles.[4]

(1) (a) Porter, R. F.; Rees, W. W.; Frauenglass, E.; Wilgus, H. S., III; Nawn, G. H.; Chiesa, P. P.; Gates, J. W., Jr. *J. Org. Chem.* **1964**, *29*, 588. (b) Wilgus, H. S., III; Frauenglass, E.; Jones, E. T.; Porter, R. F.; Gates, J. W., Jr. *Ibid.* **1964**, *29*, 594 and references cited therein.

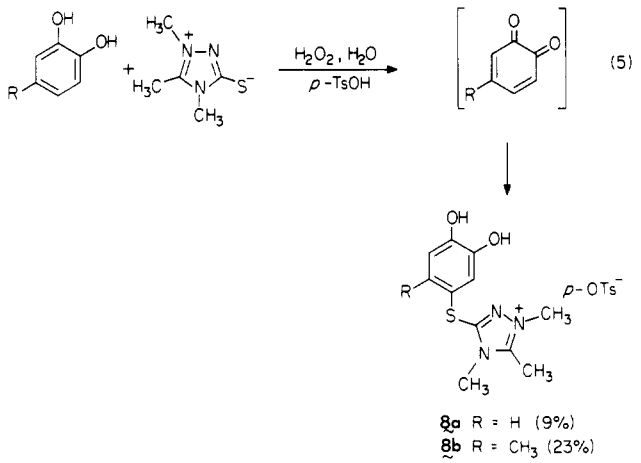
(2) Potts, K. T.; Roy, S. K.; Jones, D. P. *J. Org. Chem.* **1967**, *32*, 2245.

(3) Youngblood, M. P., manuscript in preparation. This paper discusses in detail the kinetics and mechanisms of redox reactions of (triazoliothio)-1,4-hydroquinone salts with 1,4-benzoquinones.

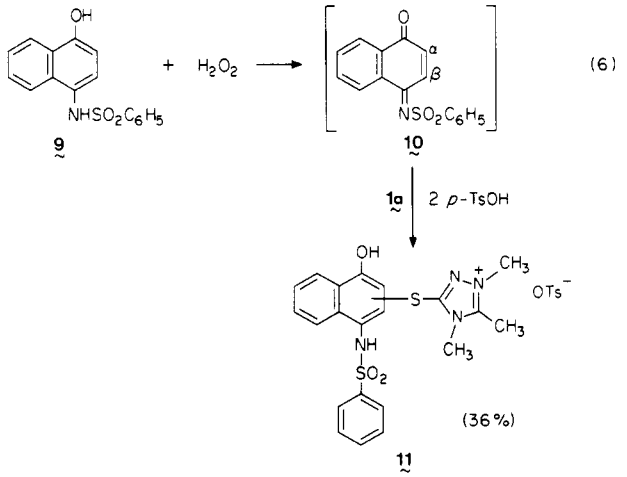
0022-3263/85/1950-0433$01.50/0



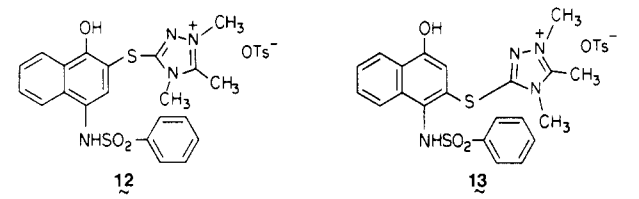
Hydrogen peroxide (30%) was added slowly to a stirred aqueous solution of triazolium thiolate **1a**, *p*-toluenesulfonic acid, and either catechol or 4-methylcatechol. The deep red *o*-quinone color formed almost immediately and then slowly disappeared as the nascent quinone was trapped by **1a** to form the catechol adducts **8** (reaction 5).

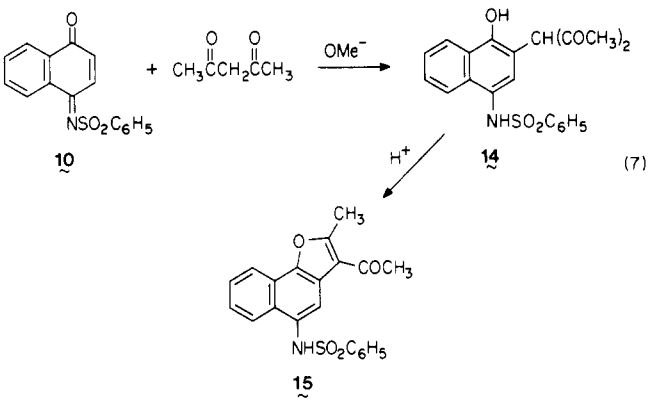


Triazolium thiolates add to 1,4-quinone imine derivatives to form 1,4-hydroquinone imine adducts. After 4-(benzenesulfonamido)naphthol (**9**) was oxidized in situ to **10**[5] with hydrogen peroxide, triazolium thiolate **1a** (which does not oxidatively dimerize because it is already highly oxidized[2]) underwent a 1,4-addition in the presence of 2 equiv of *p*-toluenesulfonic acid (reaction 6). The 1,4-hydroquinone imine adduct **11** was isolated in 36% yield.

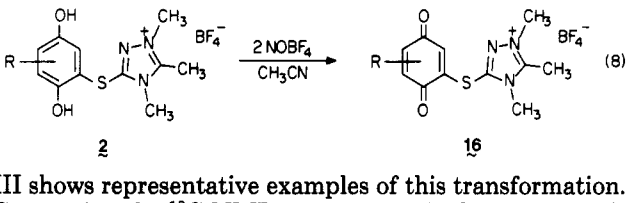


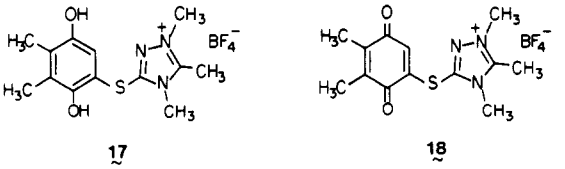
The location of the Michael attack is unclear. Because the (benzenesulfonyl)imino group is probably more electron withdrawing than the carbonyl group in **10**, the 1,4-addition of the triazolium thiolate probably occurs on the α-carbon to give adduct **12** instead of **13**. Steric considerations also favor formation of adduct **12**. An analogy comes from the work of Adams and Whitaker,[6] who reported the base-catalyzed addition of acetylacetone to **10** to form the adduct **14**. This adduct underwent acid-catalyzed cyclization to form the corresponding benzofuran **15** (reaction 7).





The (triazoliothio)hydroquinone tetrafluoroborates **2** are rapidly oxidized with 2 equiv of nitrosonium tetrafluoroborate in acetonitrile to form yellow crystalline (triazoliothio)quinone tetrafluoroborates **16** (reaction 8). Table III shows representative examples of this transformation. Comparing the ^{13}C NMR spectrum of hydroquinone adduct **17** with that of the oxidized (quinone) form **18** shows that quinone carbonyl carbons of **18** have been shifted downfield to 183.95 and 182.78 ppm from ca. 150 ppm, the region in which the carbons attached to the hydroquinone hydroxyls in **17** resonate.

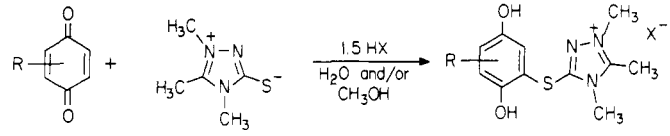




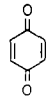
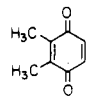
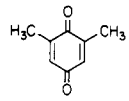
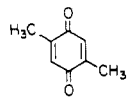
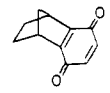
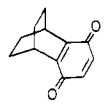
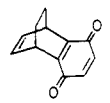
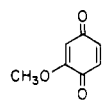
In summary, triazolium thiolates readily undergo 1,4-additions to quinones (or to quinone imines) in the presence of a protic acid. We also document one example of the addition of a tetrazolium thiolate[7] to a quinone in the presence of a protic acid. The electrochemical properties of these (triazoliothio)hydroquinones[3] as well as the ki-

(4) Finley, K. T. In "The Chemistry of the Quinonoid Compounds"; Patai, S., Ed.; Wiley: New York, 1974; pp 899ff.
(5) Adams, R.; Wankel, R. A. *J. Am. Chem. Soc.* **1951**, *73*, 131.
(6) Adams, R.; Whitaker, L. *J. Am. Chem. Soc.* **1956**, *78*, 658.
(7) Bartels-Keith, J. R.; Burgess, M. T.; Stevenson, J. M. *J. Org. Chem.* **1977**, *42*, 3725.

Table I. 1,4,5-Trimethyl-1,2,4-triazolium-3-thiolate Adducts with 1,4-Benzoquinones



1 2

quinone	X	yield, %[a]	mp, °C[b]	anal.[c] found (calcd) C	H	N
	TsO[d]	59	194–195	50.8 (51.0)	5.0 (5.0)	9.8 (9.7)
	CF_3CO_2	75	137–138	42.4 (42.7)	3.8 (3.8)	11.5 (11.5)
	TsO[d]	16	194–195	52.8 (53.2)	5.7 (5.5)	9.0 (9.3)
	BF_4	48	191–193 dec	41.8 (41.5)[e]	4.9 (5.1)	11.2 (11.2)
	CF_3CO_2	46	214–215 dec	45.4 (45.8)	4.7 (4.6)	10.4 (10.7)
	TsO[d]	40	180–181	52.8 (53.2)	5.8 (5.5)	9.2 (9.3)
	TsO[d]	58	214–215	53.2 (53.2)	5.7 (5.5)	9.3 (9.3)
	TsO[d]	53	126–128	53.9 (54.0)	5.6 (5.6)	8.4 (8.3)
	BF_4	12	207–209	47.2 (47.4)	5.0 (4.9)	10.4 (10.4)
	TsO[d]	80	183–184	57.3 (57.5)	5.5 (5.4)	8.7 (8.4)
	BF_4	78	97–98	46.7 (46.9)[f]	5.1 (5.1)	9.9 (9.7)
	TsO[d]	43	127	55.9 (56.2)[e]	5.9 (5.8)	7.8 (8.2)
	BF_4	45	190–191	48.6 (48.7)	5.4 (5.3)	10.2 (10.0)
	TsO[d]	78[g]	94–96	46.2 (46.5)[h]	5.4 (5.5)	8.5 (8.6)

[a] Based on the parent 1,4-benzoquinone. [b] Salts purified with ethanol, aqueous ethanol, or methanol/diethyl ether. [c] Satisfactory C, H, and N analyses (±0.4%) were reported for all compound. [d] *p*-Toluenesulfonate. [e] Analysis for hemihydrate. [f] Analysis for monohydrate. [g] Methoxyl group para to the triazoliumthio moiety. [h] Analysis for dihydrate.

netics and mechanisms of the nucleophilic displacement of triazolium thiolates from oxidized hydroquinone adducts[8] will be documented in separate papers.

Experimental Section

The triazolium thiolates were prepared by cyclization of the appropriate thiosemicarbazides according to published procedures.[2,9] The quinones used to prepare the (triazoliothio)-hydroquinones cited in this paper were prepared by standard literature procedures.[10] Mass spectra were determined with a Hitachi Perkin-Elmer RMS-4, Du Pont 21-491, MAT 731, or CEC Du Pont 21-110 spectrometer. ^1H NMR spectra were measured with a Varian Associates A60, Perkin-Elmer R-32 (90 MHz), or JEOL JNM-FX270 NMR spectrometer. ^{13}C NMR spectra were obtained with a JEOL FX60Q spectrometer. All NMR spectra were determined in Me_2SO-d_6 with Me_4Si as the internal standard. All of the compounds in the tables gave satisfactory mass and ^1H NMR spectra.

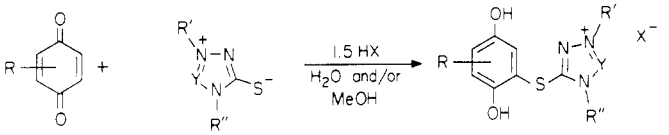
Representative Quinone Synthesis Illustrated for 2-Methoxy-*p*-benzoquinone. Potassium carbonate (27.6 g, 0.20 mol) and then silver oxide (46.4 g, 0.20 mol) were added to a stirred suspension of 2-methoxy-*p*-hydroquinone (14.0 g, 0.10 mol) in benzene (200 mL). The suspension was stirred for 2 h at ambient temperature. The solids were removed by filtration, and the filtrate was evaporated to dryness, leaving a yellow solid. This solid was crystallized from EtOAc to give yellow crystals (7.8 g, 56%): mp 145–146 °C; M_r calcd for $C_7H_6O_3$ 138, found (MS) 138. Anal. Calcd for $C_7H_6O_3$: C, 60.9; H, 4.4. Found: C, 60.6; H, 4.4.

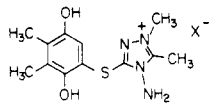
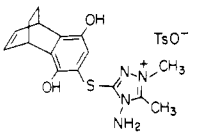
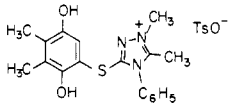
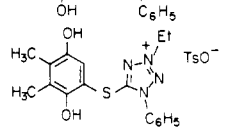
Representative (Triazoliothio)hydroquinone Salt 2 Synthesis Illustrated by the Addition of Triazolium Thiolate 1a to 2-Methoxy-*p*-benzoquinone. Triazolium thiolate **1a** (8.0 g, 0.056 mol) was added to a stirred methanol (150 mL) suspension of 2-methoxy-*p*-benzoquinone (6.4 g, 0.046 mol). To this stirred mixture was added *p*-TsOH (17.5 g, 0.092 mol), and the orange mixture was stirred at room temperature (N_2) for 24 h. The solvent was evaporated under reduced pressure to give a gray solid, which was stirred in H_2O (200 mL) to yield a colorless solid (16.2 g, 78%): mp 94–96 °C; ^1H NMR δ 2.26 (s, 3 H, $C_6H_4CH_3$), 2.63 (s, 3 H, $=CCH_3$), 3.64 (s, 3 H, $>NCH_3$), 3.69 (s, 3 H, OCH_3), 3.84 (s, 3 H, $=N^+CH_3$), 6.62 (s, 1 H, ArH), 6.83 (s, 1 H, ArH). Anal. Calcd for $C_{19}H_{23}N_3O_6S_2 \cdot 2H_2O$: C, 46.5; H, 5.5; N, 8.6; S, 13.1. Found: C, 46.2; H, 5.4; N, 8.5; S, 13.1.

1,4-Addition of Triazolium Thiolate 1a to 1,2-Naphthoquinone in the Presence of *p*-Toluenesulfonic Acid. Salt 3. A suspension of 1,2-naphthoquinone (15.8 g, 0.1 mol), triazolium thiolate **1a** (15.7 g, 0.11 mol), and *p*-TsOH (38.0 g, 0.2 mol) in distilled H_2O (200 mL) was stirred at room temperature for 18 h (N_2). The deep red tar that separated initially changed to a red solid during the 18 h. The solid was washed with distilled

(8) Youngblood, M. P.; Adin, A.; Altland, H. W., manuscript in preparation.
(9) Ollis, W. D.; Rowson, G. P. *Chem. Commun.* **1976**, 440.
(10) (a) Jurd, L. *Aust. J. Chem.* **1978**, *31*, 347. (b) Ho, T. L. *Synth. Commun.* **1979**, *9*, 237. (c) Diels, O.; Alder, K. *Chem. Ber.* **1929**, *62*, 2337.

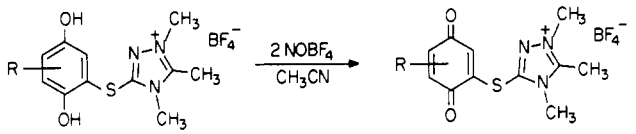
Table II. Azolium Thiolate Adducts with 1,4-Benzoquinones



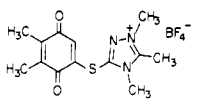
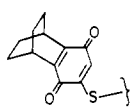
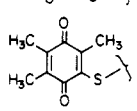
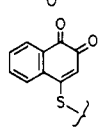
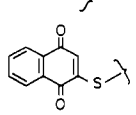
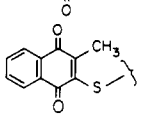
product	X	yield, %[a]	mp, °C[b]	anal.[c] found (calcd) C	H	N
	TsO^d	84	250–251 dec	50.2 (50.4)	5.3 (5.3)	12.1 (12.4)
	BF_4	63	197–198	39.0 (39.1)	4.7 (4.6)	15.5 (15.2)
		55	133–134	53.3 (53.1)	5.3 (5.4)	10.9 (10.8)
		33	214	56.6 (56.5)[e]	5.2 (5.6)	8.0 (7.9)
		52	104	54.2 (54.1)[e]	5.2 (5.3)	10.4 (10.5)

[a] Yield based on parent 1,4-benzoquinone. [b] Salts purified with methanol/ethyl ether, ethyl acetate, or ethanol/ethyl ether. [c] All compounds gave satisfactory C, H, and N analyses. [d] *p*-Toluenesulfonate. [e] Analysis for monohydrate.

Table III. (Triazoliothio)quinone or -naphthoquinone Tetrafluoroborates



2 16

product	yield, %	mp, °C	anal.[a] found (calcd) C	H	N
	37[b]	151–153	42.6 (42.8)	4.6 (4.4)	11.6 (11.5)
	79[b]	215–216	48.7 (48.9)	5.0 (4.8)	10.3 (10.1)
	71[b]	165–166	44.2 (44.3)	4.8 (4.8)	8.9 (8.5)
	46[c]	226–227 dec	46.1 (46.5)	3.7 (3.6)	10.9 (10.9)
	66[b]	197–199	45.8 (45.5)[d]	3.7 (3.8)	10.9 (10.6)
	38[b]	158–159	46.2 (45.8)[e]	4.1 (4.3)	10.1 (10.0)

[a] Satisfactory C, H, and N analyses (0.4%) were reported for all compounds. [b] Crystallized from acetonitrile/diethyl ether. [c] Crystallized from acetonitrile. [d] Analysis for hemihydrate. [e] Analysis for monohydrate.

H_2O, dissolved in MeOH, and precipitated with Et_2O. This precipitation procedure was repeated twice. The now light brown salt was vigorously stirred in EtOH for 5 min and isolated by filtration. This procedure was repeated twice. The resulting ivory colored salt was washed with EtOH and then with Et_2O: yield 19.8 g (42%); mp 208–209 °C dec; mass spectrum, m/e 302 [M – (*p*-TsOH) – 1)]$^+$, 172 [*p*-TsOH]$^+$; ^{1}H NMR δ 2.31 (s, 3 H, $ArCH_3$), 2.68 (s, 3 H, $=CCH_3$), 3.79 (s, 3 H, $>NCH_3$), 3.83 (s, 3

H, $=N^+CH_3$), 7.12 (d, J = 8 Hz, 2 H, ArH), 7.48 (m, 4 H, ArH), 7.70 (s, 1 H, ArH), 8.16 (d, J = 8 Hz, 2 H, ArH), 9.79 (s, 1 H, OH), 9.87 (s, 1 H, OH). Anal. Calcd for $C_{22}H_{23}N_3O_5S_2$: C, 55.8; H, 4.9; N, 8.9; S, 13.6. Found: C, 55.6; H, 5.0; N, 8.9; S, 13.4.

1,4-Addition of Triazolium Thiolate 1a to 1,4-Naphthoquinone in the Presence of *p*-Toluenesulfonic Acid. Salt 4. The procedure was the same as for salt **3**. Salt **4** was obtained (35.2 g, 74%) after trituration with EtOH: mp 182 °C; ^1H NMR δ 2.31 (s, 3 H, $ArCH_3$), 2.73 (s, 3 H, $=CCH_3$), 3.74 (s, 3 H, $>NCH_3$), 3.94 (s, 3 H, $=N^+CH_3$), 6.80 (s, 1 H, ArH), 7.13 (d, J = 8 Hz, 2 H, ArH), 7.51 (m, 4 H, ArH), 8.13 (m, 2 H, ArH), 9.68 (s, 1 H, OH), 9.95 (s, 1 H, OH). Anal. Calcd for $C_{22}H_{23}N_3O_5S_2 \cdot 0.25H_2O$: C, 55.3; H, 4.9; N, 8.8; S, 13.4. Found: C, 55.3; H, 5.0; N, 9.1; S, 13.8.

Bis(triazolium thiolate) Adduct 6. Triazolium thiolate **1a** (31.5 g, 0.22 mol) was added to a stirred aqueous (200 mL) suspension of *p*-benzoquinone (21.6 g, 0.20 mol). The red suspension was cooled to 5 °C, and 49% aqueous HBF_4 (70.2 g, 0.40 mol) was added dropwise. The solution was stirred at room temperature (N_2) for 18 h. The tan precipitate was collected and triturated with MeOH (100 mL) to give a colorless solid (1.0 g, 1.6%): mp 281 °C dec; ^1H NMR δ 2.68 (s, 6 H, $=CCH_3$), 3.68 (s, 6 H, $>NCH_3$), 3.90 (s, 6 H, $=N^+CH_3$), 6.92 (s, 2 H, ArH). Anal. Calcd for $C_{16}H_{22}N_6O_2S_2B_2F_8$: C, 33.8; H, 3.9; N, 14.8; S, 11.3; B, 3.8; F, 26.8. Found: C, 34.3; H, 4.0; N, 15.0; S, 11.8; B, 3.4; F, 26.5.

Mono(triazolium thiolate) Adduct 5. Aqueous HBF_4 (49%, 70.2 g, 0.40 mol) was added to a stirred aqueous (300 mL) solution of triazolium thiolate **1a** (31.5 g, 0.22 mol). *p*-Benzoquinone (21.6 g, 0.20 mol) was added slowly, and the orange solution was stirred at room temperature (N_2) for 18 h. The colorless solid that separated was collected (48.2 g, 71%): mp 162 °C; mass spectrum, m/e 252 (calcd for cation 252); ^1H NMR δ 2.68 (s, 3 H, $=CCH_3$), 3.68 (s, 3 H, $>NCH_3$), 3.89 (s, 3 H, $=N^+CH_3$), 6.70 (m, 3 H, ArH), 9.04 (s, 1 H, OH), 9.68 (s, 1 H, OH). Anal. Calcd for $C_{11}H_{14}BF_4N_3O_2S$: C, 39.0; H, 4.2; N, 12.4; S, 9.5; B, 3.1; F, 22.4. Found: C, 39.2; H, 4.2; N, 12.5; S, 9.5; B, 3.2; F, 22.6.

Addition of Triazolium Thiolate 1a to 4-Methyl-*o*-benzoquinone (Generated in Situ from the Catechol with Hydrogen Peroxide) in the Presence of *p*-Toluenesulfonic Acid. Salt 8b. H_2O_2 (30%, 3.4 g, 0.03 mol) was added to a stirred aqueous (25 mL) solution of triazolium thiolate **1a** (4.3 g, 0.03 mol), 4-methylcatechol (3.7 g, 0.03 mol), and *p*-TsOH (5.9 g, 0.031 mol). The solution was stirred at room temperature for 3 h. During this time, the deep red color of nascent *o*-quinone formed and then slowly disappeared. Absolute EtOH was added to the stirred solution, and a pale tan solid (3.0 g, 23%) slowly crystallized at room temperature: mp 220–222 °C dec; ^1H NMR δ 2.21 (s, 3 H, $ArCH_3$) 2.24 (s, 3 H, $ArCH_3$), 2.62 (s, 3 H, $=CCH_3$), 3.62 (s, 3 H, $>NCH_3$), 3.83 (s, 3 H, $=N^+CH_3$), 6.76 (s, 1 H, ArH), 6.95 (s, 1 H, ArH), 7.25 (q, 4 H, SO_3ArH). Anal. Calcd for $C_{19}H_{23}N_3O_5S_2 \cdot H_2O$: C, 51.1; H, 5.6; N, 9.4; S, 14.4. Found: C, 51.4; H, 5.3; N, 9.2; S, 14.2.

Triazolium Thiolate 1a Addition to 1,4-Naphthoquinone Monobenzenesulfonimide 10 in the Presence of *p*-Toluenesulfonic Acid. Salt 11. H_2O_2 (30%, 6.2 g, 0.055 mol) was added to a stirred MeOH (300 mL) solution of **9**[5] (15.0 g, 0.05 mol). The orange solution was stirred (N_2) at room temperature for 2 h. Triazolium thiolate **1a** (7.8 g, 0.055 mol) and then *p*-TsOH (19.0 g, 0.10 mol) were added while the temperature of the stirred mixture was kept below 20 °C. This orange mixture was stirred at room temperature (N_2) for 18 h. The solution was poured into H_2O (1 L), and the white precipitate was triturated with MeOH (100 mL) and then with Et_2O (1 L) to give a colorless powder (10.9 g, 35%): mp 196 °C; mass spectrum, m/e 441 (calcd for cation 441); ^1H NMR δ 2.28 (s, 3 H, $C_6H_4CH_3$), 2.71 (s, 3 H, $=CCH_3$), 3.68 (s, 3 H, $>NCH_3$), 3.88 (s, 3 H, $=N^+CH_3$), 7.08 (s, 1 H, naphth-H), 7.32 (q, 4 H, $CH_3C_6H_4$), 7.55 (m, 7 H, ArH), 7.94 (m, 1 H, peri-H), 8.26 (m, 1 H, peri-H). Anal. Calcd for $C_{28}H_{28}N_4O_6S_3$: C, 54.8; H, 4.6; N, 9.1; S, 15.7. Found: C, 54.5; H, 4.6; N, 9.0; S, 15.9.

Representative Preparation of (Triazoliothio)quinone Tetrafluoroborates Illustrated for Salt 18. Nitrosonium tetrafluoroborate (3.3 g, 0.028 mol) was added rapidly to a stirred CH_3CN (150 mL) solution of the corresponding hydroquinone tetrafluoroborate **17** (5.0 g, 0.014 mol). After initial fuming of a brown gas (NO_2), the solution turned clear bronze and was stirred at room temperature (N_2) for 3 h. Undissolved solid was removed by filtration, and the filtrate was concentrated to about a fourth of its volume. Et_2O was added to this stirred concentrate until a slight cloudiness resulted. A yellow crystalline solid soon separated (1.9 g, 37%): mp 151–153 °C. Anal. Calcd for $C_{13}H_{16}BF_4N_3O_2S$: C, 42.8; H, 4.4; N, 11.5. Found: C, 42.6; H, 4.6, N, 11.6.

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Registry No. **1**, 17370-06-8; **1** (R = NH_2), 61230-66-8; **1** (R = C_6H_5), 40727-03-5; **2** (R = CH_3, R′ = 2,4-$(CH_3)_2$, X = TsO), 88305-25-3; **2** (R = CH_3, R′ = 3,6-$(CH_3)_2$, X = TsO), 88305-34-4; **2** (R = CH_3, X = TsO) 5,8-methanotetrahydro-1,4-naphthohydroquinone deriv., 92593-52-7; **2** (R = CH_3, X = BF_4) 5,8-methanotetrahydro-1,4-naphthohydroquinone deriv., 92593-53-8; **2** (R = CH_3, X = TsO) 5,8-ethanodihydro-1,4-naphthohydroquinone deriv., 92593-55-0; **2** (R = CH_3, X = BF_4) 5,8-ethanodihydro-1,4-naphthohydroquinone deriv., 92593-56-1; **2** (R = CH_3, X = TsO) 5,8-ethanotetrahydro-1,4-naphthohydroquinone deriv., 92627-68-4; **2** (R = CH_3, X = BF_4) 5,8-ethanotetrahydro-1,4-naphthohydroquinone deriv., 92593-46-9; **2** (R = CH_3, R′ = 4-OCH_3, X = TsO), 88305-52-6; **2** (R = NH_2, R′ = 3,4-$(CH_3)_2$, X = TsO), 88305-42-4; **2** (R = NH_2, R′ = 3,4-$(CH_3)_2$, X = BF_4), 88305-43-5; **2** (R = NH_2, X = TsO) 5,8-ethanodihydro-1,4-naphthohydroquinone deriv., 94324-54-6; **2** (R = C_6H_5, R′ = 3,4-$(CH_3)_2$, X = TsO), 88305-54-8; **2** (R′ = 3,4-$(CH_3)_2$, X = TsO) 1-phenyl-3-ethyl-1*H*-tetrazolium deriv., 88305-48-0; **2** (R = CH_3, R′ = 2,4,5-$(CH_3)_3$, X = BF_4), 94324-56-8; **3**, 88305-18-4; **3**·BF_4^-, 88305-19-5; **3**·BF_4^- (quinone), 94324-48-8; **4**, 94324-36-4; **4**·BF_4^-, 94324-57-9; **4**·BF_4^- (3-methylhydroquinone), 94324-59-1; **4**·BF_4^- (quinone), 94324-50-2; **4**·BF_4^- (3-methylquinone), 94324-52-4; **5**, 88305-36-6; **5**·TsO^-, 88305-37-7; **5**·$CF_3CO_2^-$, 88305-38-8; **6**, 88305-50-4; **7**, 94324-38-6; **8a**, 94324-40-0; **8b**, 88305-40-2; **9**, 36942-42-4; **10**, 6009-31-0; **12**, 88305-56-0; **16** 5,8-ethanotetrahydro-1,4-naphthoquinone deriv., 94324-44-4; **16** (R = 2,4,5-$(CH_3)_3$), 94324-46-6; **17**, 92593-47-0; **17**·TsO^-, 88305-31-1; **17**·$CF_3CO_2^-$, 88305-32-2; **18**, 94324-42-2; *p*-benzoquinone, 106-51-4; 2,3-dimethyl-*p*-benzoquinone, 526-86-3; 2,6-dimethyl-*p*-benzoquinone, 527-61-7; 2,5-dimethyl-*p*-benzoquinone, 137-18-8; 5,8-methanotetrahydro-1,4-naphthoquinone, 61632-88-0; 5,8-ethanodihydro-1,4-naphthoquinone, 91368-37-5; 5,8-ethanotetrahydro-1,4-naphthoquinone, 94324-60-4; 2-methoxy-*p*-benzoquinone, 2880-58-2; 1,2-naphthoquinone, 524-42-5; 1,4-naphthoquinone, 130-15-4; *o*-benzoquinone, 583-63-1; 4-methyl-*o*-benzoquinone, 3131-54-2; 3-ethyl-1-phenyl-1*H*-tetrazolium-5-thiolate, 62681-14-5.