Use of Thiazyl Chlorides, Alkyl Carbamates, and Thionyl Chloride To Fuse 1,2,5-Thiadiazoles to Quinones and To Oxidize, Chlorinate, and Aminate Them

Shuhao Shi, Thomas J. Katz,* Bingwei V. Yang, and Longbin Liu

Department of Chemistry, Columbia University, New York, New York 10027

Received November 16, 1994[⊗]

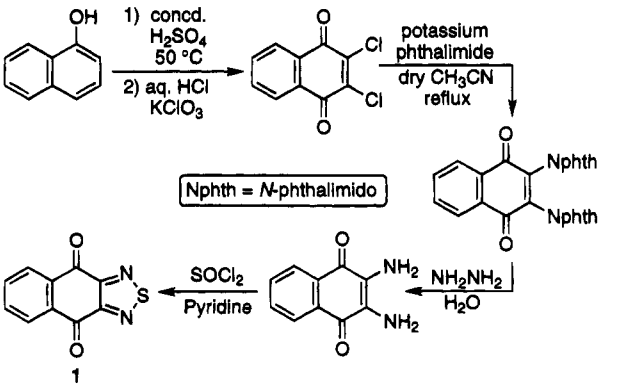
Thiazyl chlorides in a simple one-step procedure fuse 1,2,5-thiadiazole rings to quinones. So do alkyl carbamates mixed with excess thionyl chloride and pyridine. Evidence is put forward to support the hypothesis that NSCl or a related thiazyl derivative is the reactive species that brings about the transformations. Selenoyl chloride mixed with an alkyl carbamate, pyridine, and quinones similarly gives 1,2,5-selenodiazoloquinones. Thionyl chloride in pyridine chlorinates quinones and oxidizes hydroquinones. 2,3-Dichloro-1,4-quinones with S_4N_4 or with alkyl *N*-sulfinylcarbamates give 1,2,5-thiadiazoloquinones. Quinones and their 2,3-dichloro derivatives with TsNSO in pyridine give betaine derivatives of 2,3-diaminoquinones, which pyrrolidine converts into 2-amino-3-(tosylamino)quinones. A unified set of mechanisms is presented that accounts for these transformations.

Introduction

Described in this paper is a one-step procedure, using inexpensive chemicals and simple equipment, that in good yields fuses 1,2,5-thia(or selena)diazole rings to quinones. 1,2,5-Thia(or selena)diazoloquinones, which are notable in part because a number of their derivatives are conductive,[1] have usually been made by combining $SOCl_2$ or $SeOCl_2$ with 2,3-diaminoquinones,[2,3] but, as Scheme 1 illustrates for naphtho[2,3-*c*][1,2,5]thiadiazole-4,9-dione (**1**), these procedures are much longer than those described here because preparing the precursor diaminoquinones requires a number of steps.[2a,5] It is shown that the fusion of 1,2,5-thiadiazoles to quinones is brought about in excellent yields by thiazyl chlorides ($S_xN_yCl_z$),[6] reagents whose utility in organic synthesis has scarcely been studied.[6b,7]

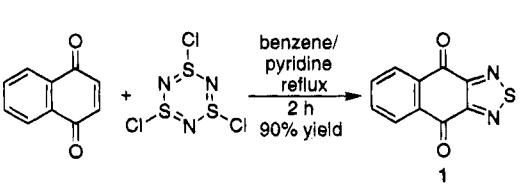
Also described are new and easy procedures for chlorinating quinones, for oxidizing hydroquinones—these use thionyl chloride as the chlorinating and oxidizing agent—and for diaminating quinones at the 2- and 3-positions.

Scheme 1



Results

Structure **1** can be made by simply combining 1,4-naphthoquinone with "trithiazyl trichloride", $(NSCl)_3$,[6,8] in benzene, or more quickly and in better yield, in benzene containing pyridine (eq 1 and Table 1, entries 15 and 16). However, the trithiazyl trichloride is somewhat painful to prepare, and it turns out there is an even easier procedure: that is to combine and reflux 1,4-naphthoquinone, ethyl carbamate (the methyl and benzyl esters work as well—see Table 1, entries 1–3), thionyl



(1)

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1995.

(1) Suzuki, T.; Kabuto, C.; Yamashita, Y.; Mukai, T.; Miyashi, T.; Saito, G. *Bull. Chem. Soc. Jpn.* **1988,** *61,* 483. (b) Suzuki, T.; Yamashita, Y.; Kabuto, C.; Miyashi, T. *J. Chem. Soc., Chem. Commun.* **1989,** 1102. (c) Ugawa, A.; Iwasaki, K.; Kawamoto, A.; Yakushi, K.; Yamashita, Y.; Suzuki, T. *Phys. Rev. B* **1991,** *43,* 14718. (d) Tsubata, Y.; Suzuki, T.; Yamashita, Y.; Mukai, T.; Miyashi, T. *Heterocycles* **1992,** *33,* 337. (e) Yamashita, Y.; Tanaka, S.; Imaeda, K.; Inokuchi, H.; Sano, M. *J. Org. Chem.* **1992,** *57,* 5517. (f) Yamashita, Y.; Miyashi, T. *Chem. Lett.* **1988,** 661.

(2) Neeff, R.; Bayer, O. *Chem. Ber.* **1957,** *90,* 1137. (b) Neidlein, R.; Tran-Viet, D.; Gieren, A.; Kokkinidis, M.; Wilckens, R.; Geserich, H.-P.; Ruppel, W. *Chem. Ber.* **1982,** *115,* 2898.

(3) Alternative procedures involve fusing the 1,2,5-thiadiazole to an appropriate benzene[4] and then oxidizing to introduce the quinone function, e.g.: (a) Cava, M. P.; Schlessinger, R. H. *Tetrahedron Lett.* **1964,** 3815. (b) Angeloni, A. S.; Ceré, V.; Dal Monte, D.; Sandri, E.; Scapini, G. *Tetrahedron* **1972,** *28,* 303. (c) Warren, J. D.; Lee, V. J.; Angier, R. B. *J. Heterocycl. Chem.* **1979,** *16,* 1617. (d) Pesin, V. G.; Belen'kaya-Lotsmanenko, I. A. *Khim. Geterotsikl. Soedin., Akad. Nauk Latev. SSR* **1965,** 354; *Chem. Abstr.* **1965,** *63,* 14851d.

(4) Weinstock, L. M.; Pollak, P. I. *Adv. Heterocycl. Chem.* **1968,** *9,* 107. (b) Kresze, G.; Maschke, A.; Albrecht, R.; Bederke, K; Patzschke, H. P.; Smalla, H.; Trede, A. *Angew. Chem., Int. Ed. Engl.* **1962,** *1,* 89. (c) Kresze, G.; Wucherpfennig, W. *Angew. Chem., Int. Ed. Engl.* **1967,** *6,* 149. (d) Pesin, V. G. *Russ. Chem. Rev.* **1970,** *39,* 923. (e) Śliwa, W.; Thomas, A. *Heterocycles* **1983,** *20,* 71.

(5) Winkelmann, E. *Tetrahedron* **1969,** *25,* 2427.

(6) Reviews of the chemistry of thiazyl halides: (a) Heal, H. G. *The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorus*; Academic Press: New York, 1980. (b) Chivers, T. *Chem. Rev.* **1985,** *85,* 341. (c) Oakley, R. T. *Progr. Inorg. Chem.* **1988,** *36,* 299.

(7) Barton, D. H. R.; Bubb, W. A. *J. Chem. Soc., Perkin Trans. 1* **1977,** 916. (b) Passmore, J.; Schriver, M. J. *Inorg. Chem.* **1988,** *27,* 2749. (c) Haas, A.; Mischo, T. *Can. J. Chem.* **1989,** *67,* 1902. (d) Apblett, A.; Chivers, T. *Can. J. Chem.* **1990,** *68,* 650. (e) Apblett, A.; Chivers, T.; Cordes, A. W.; Vollmerhaus, R. *Inorg. Chem.* **1991,** *30,* 1392. (f) Rees, C. W. *J. Heterocycl. Chem.* **1992,** *29,* 639.

(8) Jolly, W. L.; Maguire, K. D. *Inorg. Synth.* **1967,** *9,* 102.

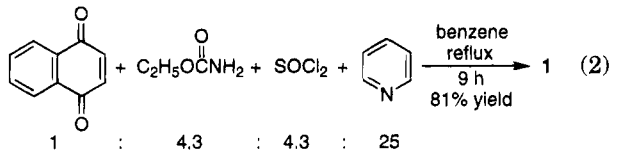
0022-3263/95/1960-1285$09.00/0

Table 1. Yields of Thiadiazole 1 Formed when 1,4-Naphthoquinone (1 mmol) Is Combined with Various Reagents in Refluxing Benzene[a]

entry	reactant (mmol)	other reactant (mmol)	mmol $SOCl_2$	mmol Py[b]	time (h)	% yield of 1	other products (%)
1	$MeOCONH_2$ (4.3)		4.3	25	9	75	
2	$EtOCONH_2$ (4.3)		4.3	25	9	80	
3	$BzlOCONH_2$ (4.3)		4.3	25	9	84	
4	EtOCONSO (4.4)			25	19	<5	NQ[c] (63)
5	EtOCONSO (4.4)	$EtOCONH_2$ (4.3)		25	24	<5	NQ (TLC anal.)
6	EtOCONSO (4.4)	$PyH^+ Cl^-$ (4.3)		25	24	<5	NQ (TLC anal.)
7	EtOCONSO (4.3)		4.3	25	4	65–74	
8	EtOCONSO (4.3)		0.8	25	12	79	
9	$EtOCONCl_2$ (3.5)	SCl_2 (2.2)		25	5	76	
10	$EtOCONCl_2$ (7.7)	S (4.4)		12.5	8	75	
11	TsNSO (4.3)		8.4	25	3[d]	81	TsCl (98)
12	TsNSO (4.7)	$POCl_3$ (8)		30	2	22	
13	TsNSO (6)	SO_2Cl_2 (7)		25	8	34	
14	$MeOCONH_2$ (4.4)	SCl_2 (7)		25	16	24	
15	$(NSCl)_3$ (2)				12	70	
16	$(NSCl)_3$ (1.25)			12.5	2	90	
17	S_4N_4 (2.5)				24	0	SM[e] (TLC anal.)
18	S_4N_4 (2.5)			25	24	0	SM (TLC anal.)[f]
19	S_4N_4 (1.25)		4.3	12.5	12	80	
20	S_4N_4 (1.25)		6		23	58	NQ (13)
21	NH_4Cl (4.5)		4.5	25	4	49	
22	NH_4Cl (9.4)	SCl_2 (10)		19	2.5	46	
23	NH_4Cl (6)	S_2Cl_2 (9)		38	16	35	
24	H_2NCONH_2 (3)		8.4	15	2	57	
25	$S_3N_2Cl_2$ (2)				13	56	NQ (6)
26	$S_3N_2Cl_2$ (2)			12.5	2.5	88	
27	S_4N_3Cl (2)			12.5	20	ca. 35	

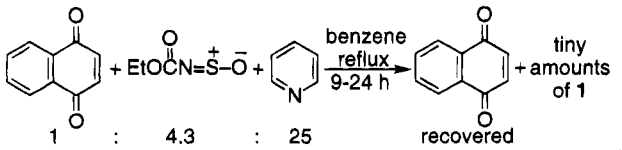
[a] 20–25 mL. [b] Pyridine. [c] 1,4-Naphthoquinone. [d] Three hours without naphthoquinone, followed by 16 h with naphthoquinone. [e] Starting material. [f] According to TLC analysis, the same experiment, but with 1,4-anthraquinone in place of 1,4-naphthoquinone, after 30 h also simply returned starting materials.

chloride, and pyridine in benzene for a few hours (eq 2). The selenium analogue is obtained as easily (in 84% yield) when $SOCl_2$ is replaced by $SeOCl_2$.



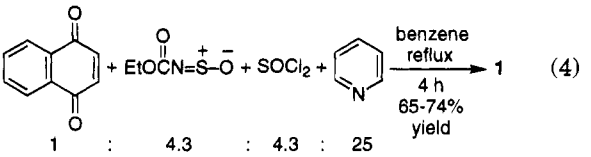
(2)

The result suggests that it is the alkyl *N*-sulfinylcarbamates (ROCONSO), which are made by combining alkyl carbamates with $SOCl_2$ and pyridine,[c,9–11] or the *N,N'*-bis(alkoxycarbonyl) sulfur diimides (ROCONSNCO$_2$R), made by combining alkyl *N*-sulfinylcarbamates with pyridine,[11] that add to the quinone. However, when ethyl *N*-sulfinylcarbamate is combined with naphthoquinone and pyridine in benzene, it does not give significant amounts of thiadiazole **1** (eq 3). To test the



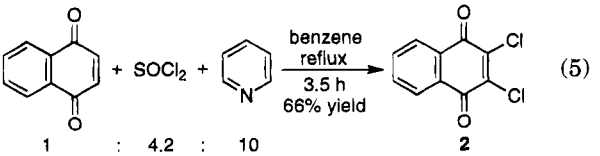
(3)

thought that single components of the reaction mixture in eq 2 if added to the reactants in eq 3 would cause the thiadiazole to form, a molar amount of the alkyl carbamate or pyridine hydrochloride was added equal to the amount of EtOCONSO. However, in neither case did the outcome change (see Table 1, entries 4–6). No significant amounts of **1** were produced. But when thionyl chloride was added to the reaction mixture, **1** did form (eq 4).



(4)

The implication is that thionyl chloride transforms either 1,4-naphthoquinone or the alkyl *N*-sulfinylcarbamate into reactive species. Accordingly, naphthoquinone was combined with thionyl chloride and pyridine in benzene, and it was discovered to give 2,3-dichloro-1,4-naphthoquinone (**2**) in good yield (eq 5).[12] Moreover,



(5)

dichloroquinone **2** combines with methyl *N*-sulfinylcarbamate and pyridine in refluxing benzene to give thiadiazole **1** (eq 6). If pyridine is omitted from the mixture, the reaction does not occur.

1,4-Naphthoquinone is not the only reactant $SOCl_2$ activates. It also combines with alkyl *N*-sulfinylcarbam-

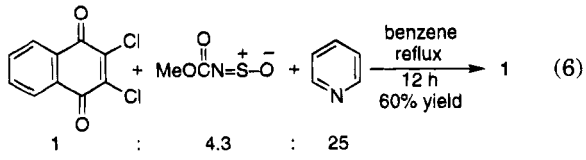
(9) Hancock, J.; Markert, A. R. *Tetrahedron Lett.* **1966**, 6157. (b) Ichimura, K.; Ichikawa, S.; Imamura, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1157. (c) Garigipati, R. S.; Freyer, A. J.; Whittle, R. R.; Weinreb, S. M. *J. Am. Chem. Soc.* **1984**, *106*, 7861. (d) Hanson, P.; Stockburn, W. A. *J. Chem. Soc., Perkin Trans. 2* **1985**, 589.

(10) Bussas, R.; Kresze, G.; Münsterer, H.; Schwöbel, A. *Sulfur Rep.* **1983**, *2*, 215.

(11) Katz, T. J.; Shi, S. *J. Org. Chem.* **1994**, *59*, 8297.

(12) This transformation relates to the discovery of Koenigs and Greiner that *N*-(1,4-dihydroxynaphthalen-2-yl)pyridinium chloride (the reaction product of naphthoquinone, pyridine, and hydrochloric acid in methanol–water) with thionyl chloride gives 2,3-dichloro-1,4-naphthoquinone.[13]

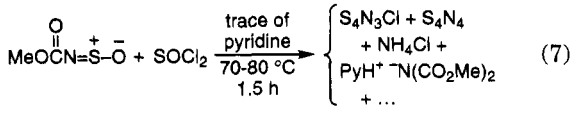
(13) Koenigs, E.; Greiner, H. *Chem. Ber.* **1931**, *64*, 1045.



(6)

ates and related molecules. Thus, when small amounts of pyridine (2 mmol) are added to a warm (70–80 °C) mixture of methyl *N*-sulfinylcarbamate (10 mmol) and thionyl chloride (10 mmol), gases evolve, leaving a brownish orange solid, from which refluxing benzene extracts S_4N_4 (1 mmol) plus sulfur. When the residue left by this extraction is warmed to 60–80 °C, pyridine·H^+ $^-N(CO_2Me)_2$ sublimes[14] leaving a yellow solid, identified by its IR and far-IR spectra to be S_4N_3Cl[15] mixed with NH_4Cl[16–18] (eq 7).

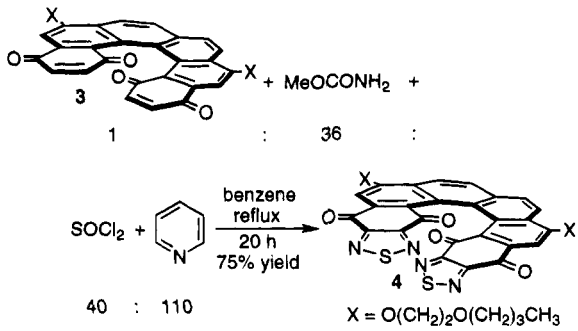
Presumably CH_3Cl and CO_2 also form, but they were not analyzed. However, their analogue (TsCl, Ts = *p*-toluenesulfonyl) was when TsNSO replaced the *N*-sulfinylcarbamate in eq 7. Thus TsNSO,[19] which when



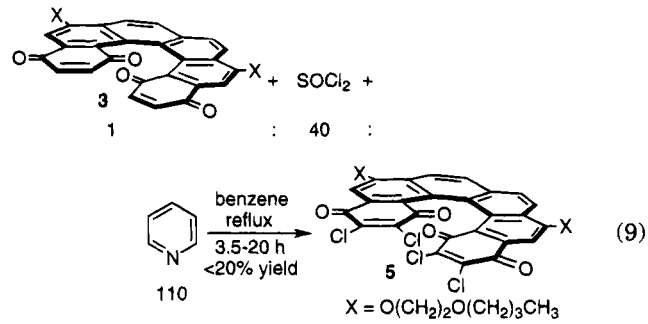
(7)

substituted in eq 4 for ethyl *N*-sulfinylcarbamate gives just as much thiadiazole **1** (64% yield in 2 h, see the Experimental Section), combines with thionyl chloride in refluxing benzene/pyridine to give (in 3 h) an almost quantitative yield of *p*-toluenesulfonyl chloride (Table 1, entry 11).[20] Moreover, the residue from this reaction both converts naphthoquinone (0.24 mol/mol of TsNSO, 16 h reaction time) into the thiadiazole in 81% yield and, after purification by extraction with hot benzene, gives pure S_4N_3Cl in 20% yield.

Reasons for favoring the hypothesis that the essential role of thionyl chloride in eq 4 is to activate the alkyl *N*-sulfinylcarbamate rather than the naphthoquinone include these observations. (1) In 4 h, the yield of **1** obtained in the procedure in eq 6 is less than 5%, only a small fraction of the ca. 70% yield of **1** obtained according to eq 4.[22] The implication is that combination of the 2,3-dichloro-1,4-naphthoquinone with the alkyl *N*-sulfinylcarbamate, since it is slower than eq 4, can not be a significant step in that equation. (2) The yield of thiadiazole **4** in eq 8 is considerably greater than the yield of the chlorinated quinone **5** in eq 9,[23] suggesting again that the chlorinated quinone is not an intermediate on the path to the thiadiazole. (3) Chlorothiazyls, including $N_3S_3Cl_3$, N_3S_4Cl, and $N_2S_3Cl_2$,[8] and combinations of reagents that plausibly generate chlorothiazyls react with



(8)



(9)

1,4-naphthoquinone in benzene /pyridine to give thiadiazole **1** (Table 1, entries 15, 16, and 25–27). These combinations include the following (Table 1, entries 9, 10, and 19–24): NH_4Cl or urea[24] and thionyl chloride; NH_4Cl and SCl_2 or S_2Cl_2;[8] S_4N_4 and 3–4 mol of thionyl chloride[25] in benzene, or better, benzene/pyridine; and EtOCON=S=NCO_2Et (generated by combining EtOCONCl$_2$ with either SCl_2 or S)[26] plus SCl_2 in benzene/pyridine.

Another set of experiments implying that thiazyl chlorides are the agents that fuse 1,2,5-thiadiazoles to the quinones are summarized in eqs 10–12. While 1,4-naphthoquinone, unlike 2,3-dichloro-1,4-naphthoquinone (eq 10), when combined with S_4N_4 for 24 h in refluxing pyridine/benzene does not give thiadiazole **1** (Table 1, entry 18), it does (eq 11) *in the presence of 2,3-dichloro-1,4-naphthoquinone*.

Similarly, boiling a benzene solution of anthracene-1,4-dione with 2 mol of S_4N_4 and 25 mol of pyridine for 30 h does not give thiadiazole **6** (TLC analysis, the starting dione remains), but as eq 12 shows, it does when 2,3-dichloro-1,4-napthoquinone in the same mixture simultaneously gives thiadiazole **1**. The implication is that combining S_4N_4 with the dichloroquinone generates a species, presumably containing S, N, and Cl, that can convert 1,4-naphthoquinone or 1,4-anthraquinone into thiadiazoles.

A related point is that the experiment analogous to eq 12, in which the 2,3-dichloro-1,4-naphthoquinone (1.0 mmol) and 1,4-anthraquinone (0.72 mmol) are refluxed

(14) Identified by its ^1H NMR, IR, and mass spectra and by its conversion by aqueous HCl into $(MeOCO)_2NH$ [(a) Akteries, B.; Jochims, J. C. *Chem. Ber.* **1986**, *119*, 83. (b) Thurber, T. C.; Townsend, L. B. *J. Heterocycl. Chem.* **1977**, *14*, 647].

(15) Nevitt, I.; Rzepa, H. S.; Woollins, J. D. *Spectrochim. Acta* **1989**, *45A*, 367.

(16) Keller, R. J. *The Sigma Library of FT-IR Spectra*, 1st ed.; Sigma Chemical Co.: St. Louis, MO, 1986; Vol. 2, p 1012c.

(17) Only two of the IR peaks observed are not in the spectra of either, at 1192 and 766 cm^{-1}.

(18) The methyl *N*-sulfinylcarbamate contains ca. 10% of methyl carbamate. Jolly and Maguire record that S_4N_3Cl is contaminated with NH_4Cl when it is prepared from $S_3N_2Cl_2$ containing SCl_2 and HCl.[8]

(19) Hori, T.; Singer, S. P.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 1456.

(20) Bussas *et al.* also noted that *p*-toluenesulfonyl chloride forms when excess thionyl chloride is not removed quickly enough during the preparation of TsNSO.[10,21]

(21) Bussas, R.; Kresze, G. *Liebigs Ann. Chem.* **1980**, 629.

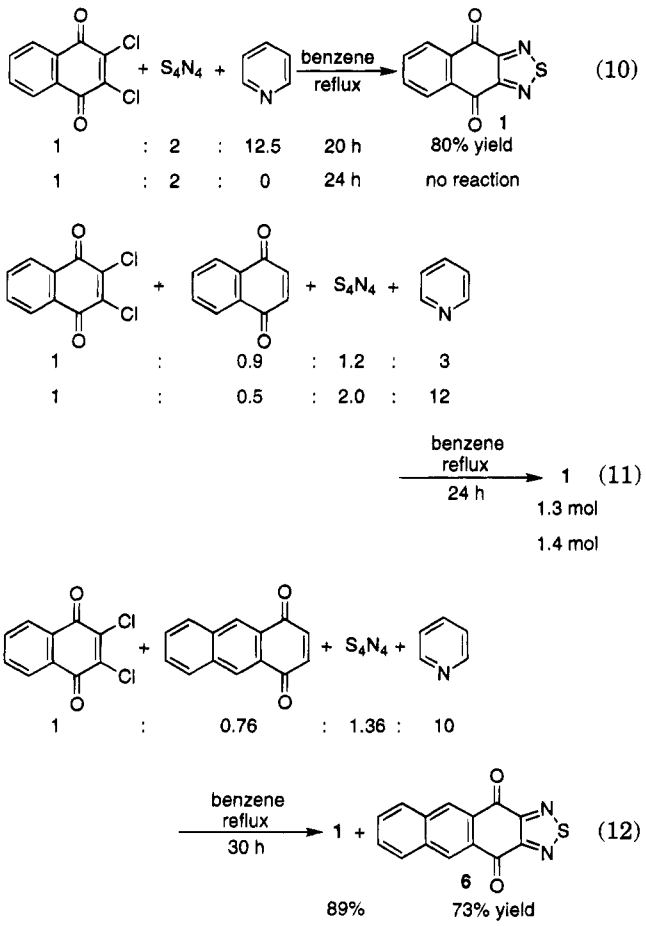
(22) Thirty percent of the dichloronaphthoquinone was recovered.

(23) The precursor, **3**, is described in: Willmore, N. D.; Liu, L.; Katz, T. J. *Angew. Chem.* **1992**, *104*, 1081; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1093.

(24) Urea + S_2Cl_2 give $S_3N_2Cl_2$: Roesky, H. W.; Schaper, W.; Petersen, O.; Müller, T. *Chem. Ber.* **1977**, *110*, 2695.

(25) Thionyl chloride plus N_4S_4 gives N_3S_4Cl: (a) *Gmelin's Handbuch der Anorganischen Chemie, Sulfur*, 8th ed.; Verlag Chemie: Weinheim, 1963; Part B, Section 3, pp 1854–1856. (b) Meuwsen, A. *Chem. Ber.* **1932**, *65*, 1724.

(26) Levchenko, E. S.; Bal'on, Ya. G.; Kirsanov, A. V. *J. Org Chem. USSR* **1967**, *3*, 2014. (b) Kresze, G.; Braxmeier, H.; Münsterer, H. *Organic Syntheses*; Wiley: New York, 1993; Collect. Vol. VIII, p 427.



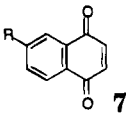
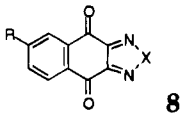
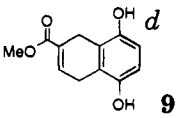
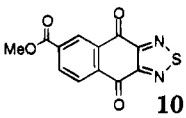
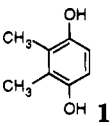
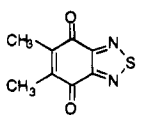
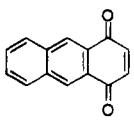
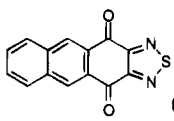
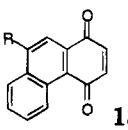
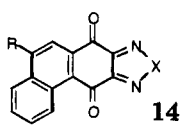
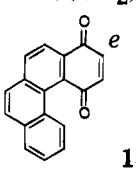
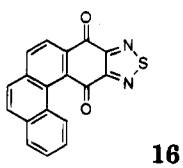
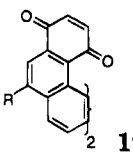
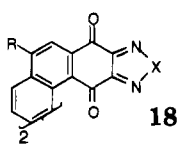
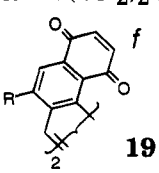
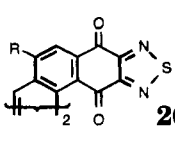
for 12 h in pyridine/benzene *not* with N_4S_4, but as in eq 6 with $C_2H_5OCONSO$ (10 mmol), *does not* give detectable amounts of **6** (TLC analysis, and none was isolable on workup). It gives **1** in 58% yield and returns 51% of the anthraquinone unchanged.

Variants of the procedures described make use of thionyl chloride's ability to effect a number of oxidations, which (see below) include oxidations of hydroquinones to quinones. As a consequence, as Table 2 shows, hydroquinones can be used in place of quinones in procedures modeled on eqs 2 and 4. Table 2 shows a variety of quinones to which 1,2,5-thia(and selena)-diazoles have been fused by the methods described here.[27]

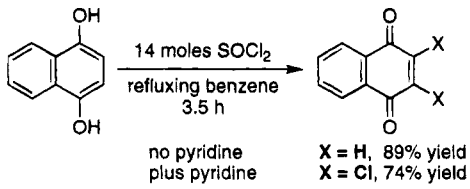
Chlorinations and Oxidations by Thionyl Chloride. The research uncovered not only a simple procedure to synthesize 1,2,5-thiadiazoloquinones, but also useful ways to chlorinate quinones and to oxidize hydroquinones. Equation 5, above, shows that thionyl chloride chlorinates quinones, a kind of transformation that may be useful in the laboratory because the reagents commonly used are very much harsher.[28] Equation 13 shows that it can also be used to oxidize hydroquinones without chlorinating them. 1,4-Dihydroxynaphthalene, when refluxed in benzene with thionyl chloride in the absence

(27) With $SeOCl_2$ as the reagent, selenium analogues of structures **20** [R = $O(CH_2)_2OBu$ and R = $O(CH_2)_{11}CH_3$] were probably also obtained, but the products were insoluble, and attempted chromatography gave only low yields (15–27%). The CH_4-CI mass spectrum of the former showed the required peaks at *m/e* = 781 and 783 (M + 1) and at 809 and 811 (M + 29). The ^1H NMR spectra of both products showed (as required) that the COCH=CHCO protons were gone, but their ^{13}C NMR spectra were not measured because the solubilities were so low, and they were not characterized further. The parent [5]helicene quinone (**19**, R = H) with CH_3CONH_2, $SOCl_2$, and pyridine in refluxing benzene also gave only uncharacterizable materials.

Table 2. Yields of 1,2,5-Thia- and Selenadiazoles Formed by Combining Quinones or Hydroquinones with Methyl Carbamate, $SOCl_2$ or $SeOCl_2$, and Pyridine in Refluxing Benzene[a]

entry	Quinone or Hydroquinone	Thia- or Selena-diazole	time (h)[b]	yield (%)
	 **7**	 **8**		
1	R = H	X = S	9	75
2	R = H	X = Se	9	84
3	R = CH_3	X = S	9	73
4	R = CN	X = S	12	82
5	1,4-Dihydroxy-naphthalene[c]	X = S, R = H	2	69
6	 *d* **9**	 **10**	12	40
7	 **11**	 **12**	40	26
8		 **6**	9	75
	 **13**	 **14**		
9	R = H	X = S	9	75
10	R = $O(CH_2)_2OBu$	X = Se	12	91
11	 *e* **15**	 **16**	7.5	38
	 **17**	 **18**		
12	R = $O(CH_2)_2OBu$	X = S	20	72
13	R = $O(CH_2)_2OBu$	X = Se	20	72
	 *f* **19**	 **20**		
14	R = $O(CH_2)_2OBu$		16	43
15	R = $O(CH_2)_{11}CH_3$		12	53

[a] Unless otherwise indicated, the molar ratios of quinone or hydroquinone, methyl carbamate, $SOCl_2$ or $SeOCl_2$, and pyridine were 1:4.3:4.3:25. [b] Reaction time. [c] For this experiment *ethyl N-sulfinyl*carbamate was used in place of *methyl* carbamate, and the molar ratios (see footnote *a*) were 1:7.5:9:33. [d] Molar ratios (see footnote *a*) 1:8:12:50. [e] Molar ratios (see footnote *a*) 1:37:40:110. [f] Molar ratios (see footnote *a*) 1:30:31:100.

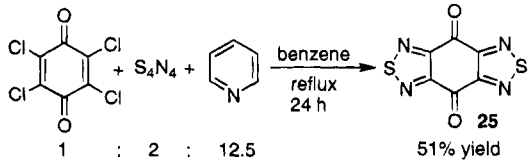


(13)

of pyridine, is oxidized in excellent yield to 1,4-naphthoquinone (eq 13). Remarkably, as the equation also shows, even if the excess of thionyl chloride is enormous, no 2,3-dichloro-1,4-naphthoquinone forms. However, when pyridine is also present, it does (Table 3 and eq 13), just as when naphthoquinone is subjected to these conditions (eq 5). These uses of thionyl chloride for chlorinations and oxidations are also effective for related structures (Table 3), although interestingly, the two 1,4-dihydroxynaphthalenes tested that were substituted in their 2-positions were not chlorinated even when pyridine was present. They were simply oxidized to the quinones (Table 3).

An observation that mechanistic accounts must explain is why the 2,3-dichloro-1,4-naphthoquinone formed from naphthoquinone according to eq 5 contains no detectable amounts of 2-chloro-1,4-naphthoquinone (TLC analysis), while that made according to the same recipe from the monochloronaphthoquinone, does. The implication is that the monochloro compound is not an intermediate on the path to the dichloro compound. Incidental observations that deserve more study are that excess sulfur dichloride in benzene/pyridine oxidizes 1,4-dihydroxy-2-methoxynaphthalene to 2-chloro-3-methoxy-1,4-naphthalenedione, while thionyl chloride gives only the unchlorinated methoxyquinone (Table 3), and that excess sulfur dichloride after 1 h in refluxing benzene/pyridine chlorinates naphthoquinone (in 71% yield) to the 2-chloro derivative.

The parent hydroquinone proved to be special both in its reaction with thionyl chloride in benzene and in its reaction with methyl carbamate and thionyl chloride in benzene/pyridine. The former gave a gel that, when dissolved in CH_2Cl_2 and passed through a silica gel chromatography column, gave back hydroquinone, suggesting that the polymeric sulfite had formed,[29] but not *p*-benzoquinone. The latter gave only uncharacterizable material. However, dithiadiazolo-*p*-benzoquinone (**25**)[2b] is formed (in 51% yield) when chloranil is combined for 24 h in benzene/pyridine with 2 mol of S_4N_4 (eq 14).



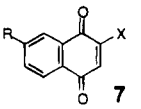
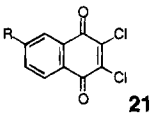
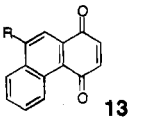
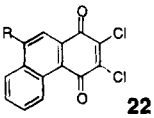
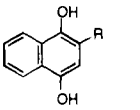
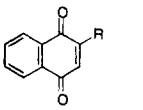
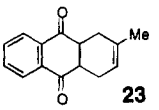
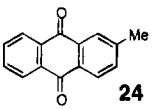
(14)

Diaminations by TsNSO in Pyridine. Another experiment showed that TsNSO, which with thionyl chloride in benzene/pyridine is an effective reagent for fusing the 1,2,5-thiadiazole ring to 1,4-naphthoquinone ($POCl_3$ and SO_2Cl_2 in place of $SOCl_2$ work too, but less well; see Table 1), in benzene/pyridine in the absence of thionyl chloride also combines with 1,4-naphthoquinone. The product, however, is not thiadiazole **1**. It is betaine **26** (Scheme 2).[30] Betaine **26** with thionyl chloride in benzene/pyridine plus either additional TsNSO or EtO-CONSO (but not without them) gives thiadiazole **1**. With pyrrolidine, the betaine gives (in ca. 72% yield) the monotoluenesulfonamide of 2,3-diamino-1,4-naphthoquinone (**27**).

Variants on these transformations were tested. In one variation, TsN=S=NTs[31] was substituted for TsNSO in the reaction with 1,4-naphthoquinone in benzene/pyridine. The product was betaine **26** (72% yield).[32] In another, 2 mol of TsN=S=NTs was used, but the pyridine was omitted. After 3 h under these conditions there was no reaction. In yet another variation, 2 mol of TsN=S=NTs was combined for 24 h in benzene with 2,3-dichloro-1,4-naphthoquinone. Again there was no reaction. And in a last variation, TsNSO (1.5 mol) was combined with 1,4-dihydroxynaphthalene in refluxing benzene. The product was 1,4-napthoquinone in 81% yield, just as when $SOCl_2$ is the oxidant.

Betaine **26** was identified by comparing it to a sample synthesized from 2,3-dichloro-1,4-naphthoquinone and

Table 3. Chlorination and Oxidation of Quinones and Hydroquinones by Thionyl Chloride in Refluxing Benzene/Pyridine[a]

entry	Quinone or Hydroquinone	product	mmol $SOCl_2$	% yield
	 **7**	 **21**		
1	R = H, X = H	R = H	14	87
2	R = H, X = Cl	R = H	4.2	88
3	R = Me, X = H	R = Me	14	66
4	R = CH_2OH, X = H	R = CH_2Cl	14	56
5	1,4-Dihydroxy-naphthalene	R = H	14	74
	 **13**	 **22**		
6		R = OMe	11	62
7		R = $O(CH_2)_2OBu$	8.5	64
				
8		R = Me	2	94
9		R = OMe	3	87
10	 **23**	 **24**	8.4	52

[a] Per mmol of quinone or hydroquinone, there were 25 mL of benzene and the following numbers of mmoles of pyridine: 25 in entries 1, 3, 4, 9, and 10; 12.5 in entries 2 and 5; 16 in entry 6; 50 in entry 7; and 4.5 in entry 8. The reaction times in hours were 3.5 in entries 1, 2, 3, and 7; 4 in entry 4; 3 in entries 5 and 6; 2 in entries 8 and 9; and 12 in entry 10.

(28) Ulrich, H.; Richter, R. *Methoden der Organischen Chemie (Houben Weyl)*; Georg Thieme Verlag: Stuttgart, 1977; Vol. VII/3a, p 140ff. (b) Ehler, K. W.; Pardini, R. S. *Org. Prep. Proc. Int.* **1983**, *15*, 157.

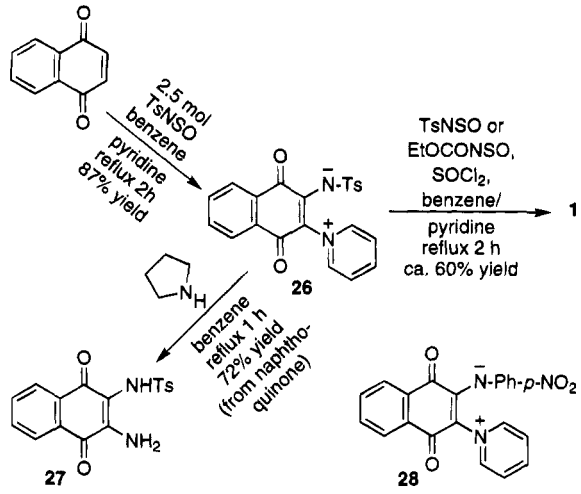
(29) The only reference to poly((oxysulfinyl)oxy-1,4-phenylene) that we could find was in: Tarumi, N.; Kimura, K; Iwahashi, H. Brit. UK Pat. Appl. GB2072535 A 811007; *Chem. Abstr.* **1982**, *96*, 208388x.

(30) Ullmann, F.; Ettisch, M. *Chem. Ber.* **1921**, *54*, 259.

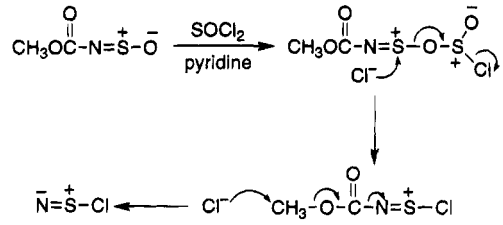
(31) Wucherpfennig, W.; Kresse, G. *Tetrahedron Lett.* **1966**, 1671.

(32) It is not surprising because TsN simply takes the role of O and because even the TsNSO used in Scheme 2 should have been converted by the pyridine into TsNSNTs.[4c,21,31]

Scheme 2



Scheme 3



$TsNH_2$ in pyridine[30] and by comparing its ^{1}HNMR spectrum and that of a known analogue (**28**).[33] The structure of **27** was assigned on the basis of its NMR and mass specta and of analogies between the conversion proposed for **26** to **27** and transformations in which secondary amines remove the carbons from other pyridinium salts.[34]

Similar experiments with 1,4-anthraquinone and 1,4-phenanthraquinone gave betaines analogous to **26** in 78% and 64% yields, respectively.[35] Pyrrolidine converted these to the analogues of aminotosylamide **27** in yields of 52% and 34%.

Discussion

Formation of Thiadiazoles and Betaines. A concise explanation for why so many, but not all, the reagents described above fuse 1,2,5-thiadiazole rings to quinones is that the effective ones are sources of thiazyl chloride (NSCl) or of related thiazyl chlorides[6] and that it (or they) brings (bring) about the transformations.

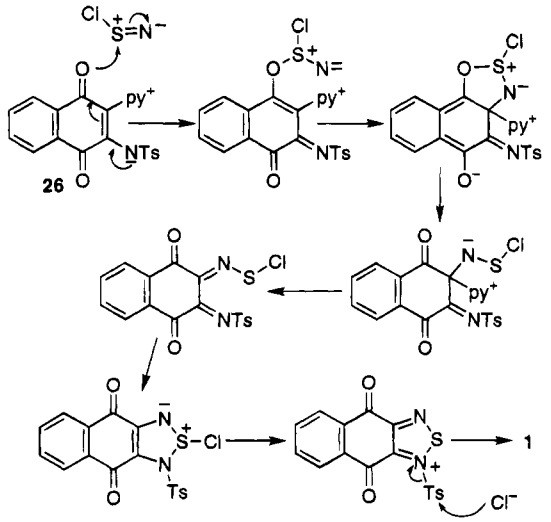
$N_3S_3Cl_3$ when warmed gently is converted into NSCl.[6,7b,36] Methyl or ethyl *N*-sulfinylcarbamates with thionyl chloride in benzene/pyridine can plausibly give thiazyl chloride as, for example, in Scheme 3, a scheme that relates somewhat to Roesky's conversion of urea and S_2Cl_2 into $S_3N_2Cl_2$.[24] *N*-Sulfinyl-*p*-toluenesulfonamide combines with thionyl chloride to give *p*-toluenesulfonyl chloride (see above and refs 10 and 21), and a formulation of this transformation similar to Scheme 3 seems reasonable, especially as S_4N_3Cl can be isolated both from this reaction product as well as from that resulting when MeOCONSO, thionyl chloride, and pyridine are mixed in benzene.[37] Moreover, S_4N_3Cl forms when S_4N_4 is mixed with thionyl chloride,[25] a combination that also converts 1,4-naphthoquinone into the thiadiazole. And S_4N_4 when combined with 2,3-dichloro-1,4-naphthoquinone plausibly generates NSCl or related materials (see eqs 10–12 and the discussion below). So should EtOCON=S=NCO_2Et and SCl_2 or urea and thionyl chloride (again by reactions patterned on Scheme 3). Moreover, ammonium chloride and S_2Cl_2 are the recommended reagents for preparing $S_3N_2Cl_2$.[8] Furthermore, the pyridine-containing solutions of all three thiazyl chlorides used in the experiments summarized in Table 1 are the green color characteristic of solutions of NSCl,[36b,38] and as Table 1 shows, the presence of pyridine improves the yields and decreases the time for reaction. This is in accord with the notion that by coordinating to them, pyridine dissociates the thiazyl chlorides.

Alternative accounts for the formation of the thiadiazoles might invoke as the key transformation cycloadditions of RN=S=NR units to the quinones, like those considered for additions of S_4N_4 to acetylenes[39] and strained olefins[40] and of related cyclothiazyl chlorides to norbornene.[41] However, these accounts are rejected because although $MeOCONH_2$ plus $SOCl_2$ in benzene/pyridine produces $MeOCONSNCO_2Me$,[11] when this structure and other materials with NSN structures were tested, they did not combine with quinones. These materials include S_4N_4, which does not react with 1,4-naphthoquinone in benzene/pyridine if $SOCl_2$ is not present, and TsNSNTs, which in boiling benzene in the absence of pyridine does not react appreciably with either 1,4-naphthoquinone or with 2,3-dichloro-1,4-naphthoquinone. If pyridine is present, TsNSNTs and both 1,4-naphthoquinone and 2,3-dichloro-1,4-naphthoquinone give betaine **26**.

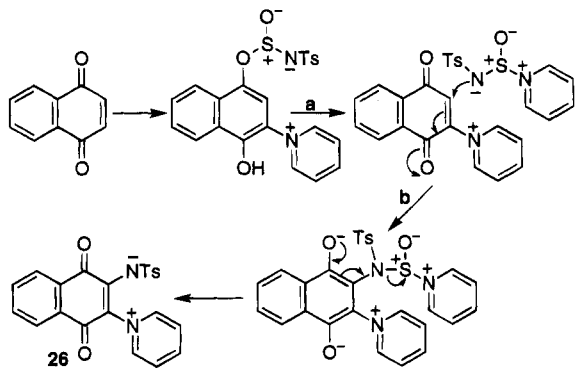
If thiazyl chlorides (or related structures) *are* the species that combine with the quinones, both reactants would be electrophiles. Thiazyl chlorides react, even in the presence of pyridine, with nucleophiles like electron-rich alkenes, phenols, and furans and not with alkenes conjugated with ketones.[7a,f,42] Accordingly, for the reactants to combine, either the thiazyl derivatives or the quinones must, presumably, first be converted by pyridine or another base into nucleophiles. Since thiazyl halides, like other derivatives of SO_2,[10] should unite with nucleophiles at their sulfur atoms, their attack as elec-

(33) Agrawal, N. L.; Schäfer, W. *J. Org. Chem.* **1980**, *45*, 5139.
(34) Rodig, O. R. In *Pyridine and Its Derivatives, Supplement, Part One*; Abramovitch, R. A., Ed.; Interscience: New York, 1974; pp 370ff. (b) Van Allan, J. A.; Reynolds, G. A. *J. Org. Chem.* **1963**, *28*, 1022.
(35) In the latter case, the regiochemistry and the regiospecificity were not determined. If the product is a mixture, the ^{1}H NMR spectrum does not show it.
(36) Glemser, O.; Richert, H. *Z. Anorg. Allgem. Chem.* **1961**, *307*, 313. (b) Patton, R. L.; Jolly, W. L. *Inorg. Chem.* **1970**, *9*, 1079.
(37) $N_3S_3Cl_3$, which is in equilibrium with NSCl (refs 36b and 7b), is easily reduced to S_4N_4, which with $SOCl_2$ gives S_4N_3Cl (ref 25).
(38) Vincent, H.; Monteil, Y. *Synth. React. Inorg. Met.-Org. Chem.* **1978**, *8*, 51.
(39) Mataka, S.; Takahashi, K.; Yamada, Y.; Tashiro, M. *J. Heterocycl. Chem.* **1979**, *16*, 1009. (b) Daley, S. T. A. K.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1987**, 203. (c) Daley, S. T. A. K.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1987**, 207. (d) Dunn, P. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1579. (e) Dunn, P. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1585.
(40) Brinkman, M. R.; Allen, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 1550. (b) Mock, W. L.; Mehrotra, I. *J. Chem. Soc., Chem. Commun.* **1976**, 123.
(41) Hazell, A. C.; Hazell, R. G.; Banister, A. J.; Fielder, A. J. *Acta Crystallogr., Sect. B: Struct. Sci.* **1981**, *B37*, 177. (b) Apblett, A.; Chivers, T.; Cordes, A. W.; Vollmerhaus, R. *Inorg. Chem.* **1991**, *30*, 1392.
(42) S_4N_4 also combines with phenols [(a) Mataka, S.; Takahashi, K.; Shiwaku, S.; Tashiro, S. *J. Chem. Res., Synop.* **1985**, 346. (b) Mataka, S. Takahashi, K.; Ikezaki, Y.; Hatta, T.; Tori-i, A.; Tashiro, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 68], although in the one example in which reactivities toward phenols were compared, it proved less reactive than two thiazyl halides (ref 7a).

Scheme 4



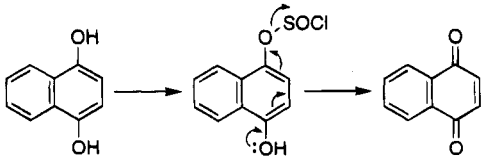
Scheme 5



trophiles on either quinones or phenolic base–adducts of quinones would not form the observed carbon–nitrogen bonds. Thus, of the two reactants, at least the thiazyl derivative probably serves, after conversion by reaction with base, as a nucleophile.

Two starting points for the formulation of mechanisms for the transformations of quinones and thiazyl derivatives into 1,2,5-thiadiazoles are this proposition and a plausible mechanism (Scheme 4) to explain the observation that betaine **26** combines with either EtOCONSO and $SOCl_2$ or TsNSO and $SOCl_2$ to give **1**.

Similar accounts can then be formulated for both the reaction of 1,4-naphthoquinone (rather than betaine **26**) with a thiazyl chloride and for the *formation* of the betaine from 1,4-naphthoquinone, pyridine, and *N*-sulfinyltosylamide. Scheme 5 presents a plausible account for this last transformation. It supposes the following: again that the *N*-sulfinyltosylamide (or the *N,N'*-tosylsulfurdiimide derived from it[43]), like other derivatives of SO_2,[10] reacts with nucleophiles at sulfur; that, as in Scheme 4, the NSX derivative adds to an unsaturated ketone as a nucleophile; and that pyridine is incorporated in a way similar to that followed when, in the presence of acid, it adds to 1,4-naphthoquinone.[44] Step a in Scheme 5 is an analogue of the formulation in eq 15 of the oxidation of 1,4-dihydroxynaphthalene by $SOCl_2$. Step b has the pyridine adduct of *N*-sulfinyltosylamide add to the quinone, an analogue of the base-catalyzed addi-

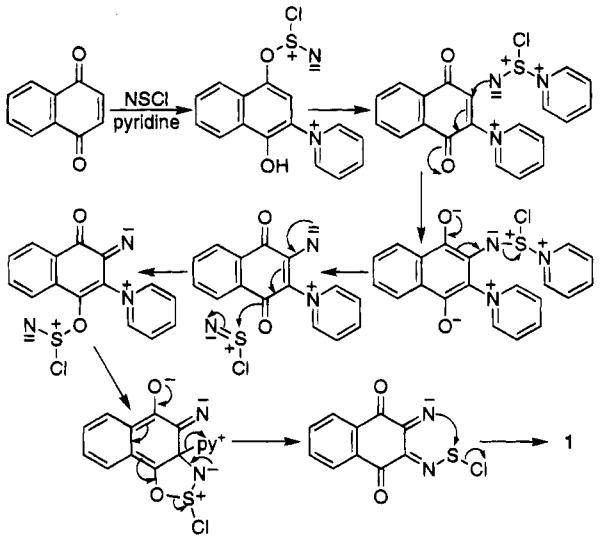


(15)

tion of a variety of *N*-sulfinyl compounds to S=O and C=O bonds.[44,45] [A variant would instead have structures related to $TsNSO^{2-}$ or TsN^{2-}, eliminated in step a, add to the quinone, and another molecule of TsNSO (or TsNSNTs) then act as an oxidant.] The next step, in which SO is lost and the quinone formed, is similar to the preceding step and eq 15. Scheme 5, incidentally, is in accord with the observation that for good yields to be achieved, more than 1 mol of TsNSO is required.[48]

The similar formulation for the reaction of naphthoquinone with the thiazyl halides, which seems to be the basis for eqs 1, 2, and 4, and for all the transformations in Tables 1 and 2, then looks like Scheme 6. (It is

Scheme 6



possible that the chlorine atoms depicted in this scheme are instead more complex residues.) A variant to account for $N_3S_3Cl_3$ combining with 1,4-naphthoquinone to give thiadiazole **1** even in the absence of pyridine (although more slowly than in its presence) is Scheme 7.

The combination of S_4N_4 with 2,3-dichloro-1,4-naphthoquinone probably involves pyridine transforming S_4N_4 into a better nucleophile, just as ammonia,[49] secondary amines, and various other nucleophiles, like KCN, Na_2S,

(43) Pyridine converts TsNSO into TsNSNTs [refs 4c (see p 165), 21, and 31]. Thus, the group attached to sulfur in Scheme 5, which for simplicity is drawn in Scheme 5 as O, might instead be NTs.

(44) Pyridine in the presence of acid adds to 1,4-naphthoquinone, see: (a) Barnett, E. de B.; Cook, J. W.; Driscoll, E. P. *J. Chem. Soc.* **1923**, *123*, 503. (b) Reference 13.

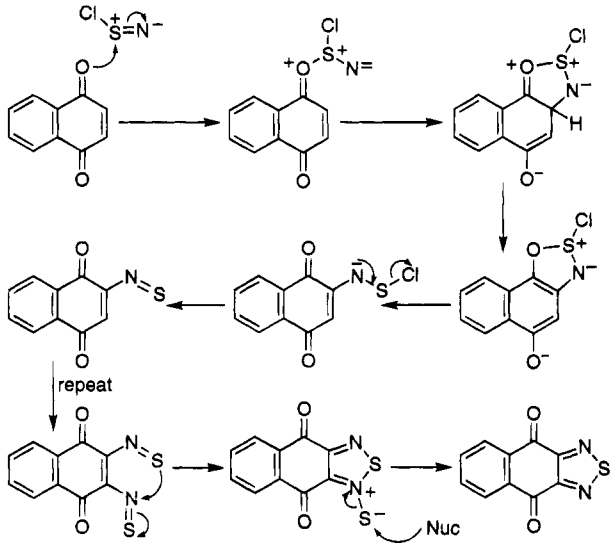
(45) Pyridine also converts XCONSO into XCONSNCOX, where X = OR (ref 11) and X = Ph (ref 46). Metal alkoxides and other strong bases convert arylNSOs into arylNSNaryls (ref 47) and condense an arylNSO with a ketone (ref 47d). Piperidine condenses arylNSOs with aldehydes (ref 47a).

(46) Levchenko, E. S.; Dorokhova, E. M. *J. Org. Chem. USSR (Engl. Transl.)* **1972**, *8*, 2573

(47) Hörhold, H.-H. *Z. Chem.* **1972**, *12*, 41. (b) Hörhold, H.-H.; Flossmann, K.-D. *Z. Chem.* **1967**, *7*, 345. (c) Minami, T.; Miki, H.; Matsumoto, H.; Ohshiro, Y.; Agawa, T. *Tetrahedron Lett.* **1968**, 3049; Hörhold, H.-H.; Beck, J. *J. Prakt. Chem.* **1969**, *311*, 621. (d) Hörhold, H.-H.; Wolf, H.; Märtin, R. *J. Prakt. Chem.* **1975**, *317*, 653. (e) Süsse, M.; Angrick, E. *Z. Chem.* **1976**, *16*, 318.

(48) In refluxing benzene, anthracene-1,4-dione, TsNSO, and pyridine in a molar ratio of 1:2.4:5 gave (in 3 h) a yield of 78% and in a ratio of 1:1.44:4 in 2 h a yield of only 37%. If the TsNSO is first converted by the pyridine into TsNSNTs, more than 2 mol of TsNSO could be required.

Scheme 7



and lithium, sodium, and potassium azides[50] convert it into $S_4N_5^-$, while ammonia,[50a] to a lesser extent, and $NaNH_2$[50a] and the azides of larger cations, to a greater extent,[50b] convert it into $S_3N_3^-$. Although too little is known to formulate the details, the simplest balanced equation accounting for the union of S_4N_4 with the dichloroquinone is eq 16. The essential point is that

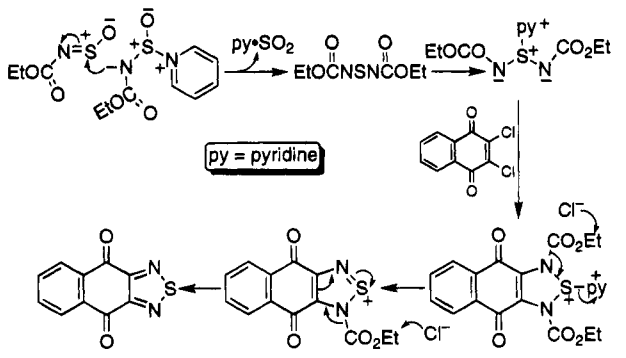
$$S_4N_4 + \text{2,3-dichloro-1,4-naphthoquinone} \rightarrow \mathbf{1} + N_2S_3Cl_2 \quad (16)$$

when thiadiazole **1** forms, a thiazyl chloride must form as well. That is why the dichloroquinone induces the reaction of S_4N_4 with 1,4-naphthoquinone (eq 11) and with 1,4-anthraquinone (eq 12).

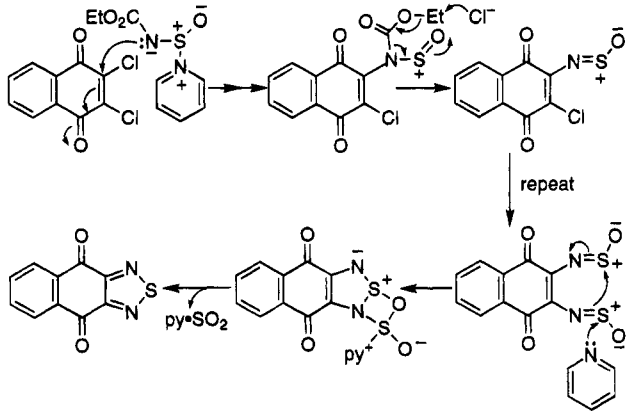
In contrast, when ethyl *N*-sulfinylcarbamate reacts with 2,3-dichloro-1,4-quinone, it should *not* generate a thiazyl chloride. This is in accord with the observation described in the Results that unlike S_4N_4, ethyl *N*-sulfinylcarbamate when it reacts with 2,3-dichloro-1,4-naphthoquinone (eq 6) does *not* induce 1,4-anthraquinone to form thiadiazole **6**. Schemes 8 and 9 present possible sequences of steps that lead to the transformation in eq 6. The former takes into account pyridine's catalyzing the conversion of alkyl *N*-sulfinylcarbamates into *N,N'*-bis(alkoxycarbonyl)sulfur diimides.[11,51] The latter is an alternative that differs from the former only in the order of the steps. The role assigned to the alkyl *N*-sulfinylcarbamate in Scheme 9 is, after union with pyridine,[52] the same as that of the *N*-sulfinyltosylamide in Scheme 5.

Oxidation and Chlorination by Thionyl Chloride. A number of examples are known of chemical reactions

Scheme 8



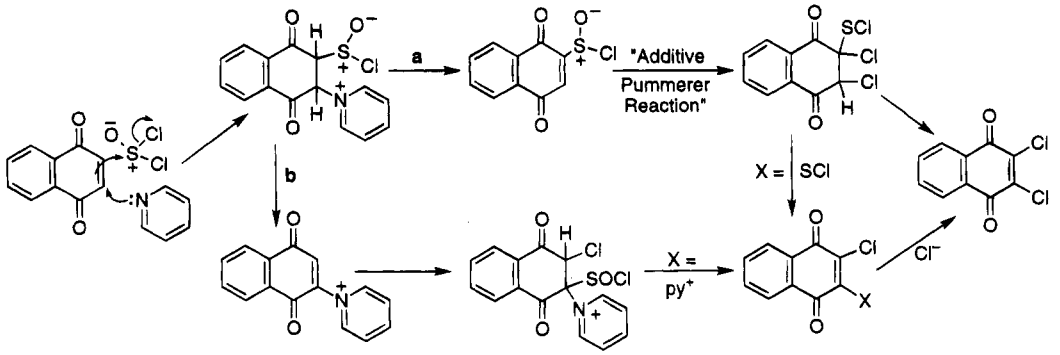
Scheme 9



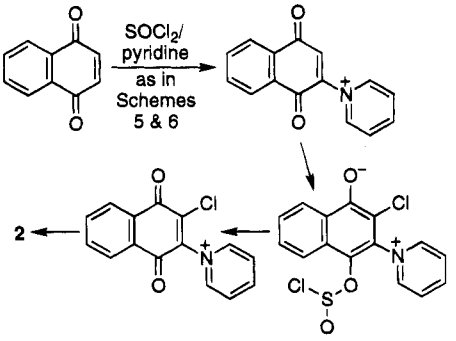
in which thionyl chloride acts as an oxidant.[55] Most closely related to those described here are Koenigs and Greiner's two-step chlorination of naphthoquinone,[13] the chlorinations of maleic anhydride, of its derivatives,[56] and of acetylene dicarboxylic acid,[57] and the chlorosulfenylation and chlorination of cinnamic and related acids.[58,59] Scheme 10 depicts steps that would account for the chlorination of naphthoquinone. Path a relates to mechanisms considered by Higa and Krubsack.[58a] It invokes transformations related to the Pummerer reaction[61] that can account for many oxidative conversions brought about by thionyl chloride. Path b relates to a mechanism considered by Relles,[56] which invokes steps accounting for oxidations of alcohols and amides.[61g,h] However,

(49) Scherer, O. J.; Wolmershäuser, G. *Chem. Ber.* **1977**, *110*, 3241.
(50) Bojes, J.; Chivers, T.; Drummond, I.; MacLean, G. *Inorg. Chem.* **1978**, *17*, 3668. (b) Bojes, J.; Chivers, T.; Oakley, R. T. *Inorg. Synth.* **1989**, *25*, 30.
(51) For pyridine·SO_2 see: Moede, J. A.; Curran, C. *J. Am. Chem. Soc.* **1949**, *71*, 852.
(52) In this scheme, pyridine converts the *N*-sulfinylcarbamate, whose reactions with alkenes identify it as an electrophile,[53,54] into a nucleophile.
(53) In Diels–Alder reactions: (a) Reference 4c and references therein. (b) Reference 9c. (c) Mock, W. L.; Nugent, R. M. *J. Am. Chem. Soc.* **1975**, *97*, 6521. (d) Mock, W. L.; Nugent, R. M. *J. Am. Chem. Soc.* **1975**, *97*, 6526.
(54) In ene reactions: (a) Kataev, E. G.; Plemenkov, V. V. *J. Org. Chem. USSR (Engl. Transl.)* **1966**, *2*, 1119. (b) Schönberger, N.; Kresze, G. *Liebigs Ann. Chem.* **1975**, 1725. (c) Deleris, G.; Kowalski, J.; Dunogues, J.; Calas, R. *Tetrahedron Lett.* **1977**, 4211. (d) Reference 19. (e) Kresze, G.; Bussas, R. *Liebigs Ann. Chem.* **1980**, 843. (f) Bussas, R.; Kresze, G. *Liebigs Ann. Chem.* **1982**, 545. (g) Deleris, G.; Dunogues, J.; Gadras, A. *Tetrahedron* **1988**, *44*, 4243. (h) Whitesell, J. K.; Carpenter, J. F.; Yaser, H. K.; Machajewski, T. *J. Am. Chem. Soc.* **1990**, *112*, 7653. (i) Whitesell, J. K.; Yaser, H. K. *J. Am. Chem. Soc.* **1991**, *113*, 3526.
(55) Davis, M.; Szkuta, H.; Krubsack, A. J. *Mech. React. Sulfur Compd.* **1970**, *5*, 1.
(56) Relles, H. M. *J. Org. Chem.* **1972**, *37*, 3630.
(57) McDonald, R. N.; Krueger, R. A. *J. Org. Chem.* **1963**, *28*, 2542.
(58) Higa, T.; Krubsack, A. J. *J. Org. Chem.* **1975**, *40*, 3037. (b) Higa, T.; Krubsack, A. J. *J. Org. Chem.* **1976**, *41*, 3399. (c) Nakagawa, S.; Okumura, J.; Sakai, F.; Hoshi, H.; Naito, T. *Tetrahedron Lett.* **1970**, 3719. (d) Wright, W. B., Jr.; Brabander, H. J. *J. Heterocycl. Chem.* **1971** *8*, 711. (e) Wright, W. B., Jr. *J. Heterocycl. Chem.* **1972**, *9*, 879.
(59) Others include oxidations of carbons adjacent to[60a,b] or vinylogous to carbonyls,[60c,d] nitriles,[60e] or the C=N's of heterocyclic rings.[60f,g] Yet others include oxidations of benzoin[60h] and of an amide.[60i]
(60) (a) Sehgal, R. K.; Krubsack, A. J. *Synth. Commun.* **1980**, *10*, 245 and references cited therein. (b) Cushman, M. Cheng, L. *J. Org. Chem.* **1978**, *43*, 3781. (c) Merchant, J. R.; Bhat, A. R.; Rege, D. V. *Tetrahedron Lett.* **1972**, 2061. (d) Oka, K.; Hara, S. *J. Org. Chem.* **1978**, *43*, 4533. (e) Ohoka, M.; Kojitani, T.; Yanagida, S.; Okahara, M.; Komori, S. *J. Org. Chem.* **1975**, *40*, 3540. (f) Graf, R.; Zettl, F. *J. Prakt. Chem.* **1936**, *147*, 188. (g) Boon, W. R. *J. Chem. Soc.* **1945**, 601. (h) Okumura, Y. *J. Org. Chem.* **1963**, *28*, 1075. (i) Büchi, G.; Lukas, G. *J. Am. Chem. Soc.* **1964**, *86*, 5654.
(61) De Lucchi, O.; Miotti, U.; Modena, G. *Org. React.* **1991**, *40*, 157.

Scheme 10



Scheme 11



Scheme 11 shows an alternative that we favor because it follows steps similar to those described above to account for a variety of other transformations: Schemes 4–7 and eq 15.

Conclusions

This study shows that 1,2,5-thiazoloquinones can be synthesized much more easily than heretofore, that thiazyl chlorides may have significant utility in organic synthesis,[62] that the combinations of alkyl carbamates and thionyl chloride may have uses that previously were not considered, that thionyl chloride may be generally useful as an agent for chlorinating quinones and oxidizing hydroquinones, and that *N*-sulfinyl-*p*-toluenesulfonamide plus pyridine diaminates quinones.

Experimental Section

The term "chromatography" specifies flash column chromatography on silica, 32–62 mm, from Woelm. Melting points were generally measured using samples purified by chromatography. Benzene was distilled from potassium. Methyl carbamate, urethane, benzyl carbamate, thionyl chloride (99+%), selenium oxychloride (97%), SCl_2 (80%, containing S_2Cl_2), *N,N*-dichlorourethane (90%), and anhydrous pyridine were purchased from Aldrich Chemical Co., Inc., and used without further purification. S_4N_4,[63] $S_3N_2Cl_2$,[24] $S_3N_3Cl_3$,[64] and S_4N_3Cl[25] were prepared by the methods cited. TsNSO was prepared by refluxing $TsNH_2$ with $SOCl_2$ for 8 h and pumping it dry, and TsNSNTs was prepared by combining this product with 2.5 mol % pyridine in benzene (1:1) and stripping the solvent.[4c] EtOCONSO and MeOCONSO were prepared from the alkyl carbamates and $SOCl_2$ in pyridine–benzene.[11]

Preparations of Thiadiazole 1 According to Table 1. Entry 1. A solution of methyl carbamate (320 mg, 4.3 mmol), thionyl chloride (0.31 mL, 4.3 mmol), and dry pyridine (2 mL, 25 mmol) in benzene (25 mL) was stirred for 30 min at room temperature, and then naphthoquinone (158 mg, 1 mmol) was added. After the solution was refluxed for 9 h, the solvent was removed, and the residue, dissolved in CH_2Cl_2, was washed (dilute HCl). Chromatography, with CH_2Cl_2 as the eluant, gave 162 mg (75% yield) of naphtho[2,3-c][1,2,5] thiadiazole-4,7-dione (**1**), a yellow solid, mp 245–246 °C (lit.[2b] mp 246.5 °C). The NMR spectra match those published:[2b] ^1H NMR (200 MHz, $CDCl_3$), δ 7.74 (dd, J = 5.8, 3.4 Hz, 2 H), 8.45 (dd, J = 5.8, 3.4 Hz, 2 H); ^{13}C NMR (75 MHz, CD_2Cl_2), δ 173.1, 153.1, 132.1, 130.4, 125.1; IR (KBr) 1680 cm^{-1}; MS (EI) *m/e* (rel int) 216 (100), 104 (64), 76 (36), 136 (29); HRMS calcd for $C_{10}H_4N_2O_2S$ 215.9994, found 216.0004.

Entries 2 and 3. The procedures, the stoichiometries, and the amounts of naphthoquinone used were the same as in entry 1.

Entry 9. The procedure is based on that of Levchenko et al. and Kresze et al.[26] Sulfur dichloride (1.6 g, 80%, containing S_2Cl_2, ca. 12.4 mmol) was added in drops to a stirring mixture of *N,N'*-dichlorourethane (3.52 g, "90% pure", ca. 20 mmol) and pyridine (1 drop) in a 25 mL round-bottomed flask. The reaction took place vigorously, and gas evolved. The liquid turned from red to pale yellow. After the addition, the mixture was heated at 60 °C under reduced pressure (15 mmHg) for 10 min. Residual volatile materials were removed by evacuating the flask at room temperature by means of an oil pump. Part of the yellow liquid (0.70 g) was refluxed with naphthoquinone (158 mg, 1 mmol) and pyridine (2 mL, 25 mmol) in benzene (35 mL) for 5 h. Workup as before gave 165 mg (76%) of **1**.

Entry 10. A mixture of sulfur (140 mg, 4.4 mmol) and *N,N'*-dichlorourethane (1 mL, "90% pure", ca. 7.7 mmol) in benzene (25 mL) was refluxed for 4 h. Naphthoquinone (158 mg, 1 mmol) and pyridine (1 mL, 12.5 mmol) were then added, and the mixture was refluxed for another 4 h. Workup as before gave 162 mg (75%) of **1**.

Entry 11. The mixture of TsNSO[4c] (915 mg, 4.2 mmol), $SOCl_2$ (1 g, 8.4 mmol), and pyridine (2 mL, 25 mmol) in benzene (25 mL) was refluxed for 3 h. The solvent was stripped, and the residue was dried at oil pump vacuum. The resulting brown solid was refluxed with naphthoquinone (158 mg, 1 mmol) in benzene (25 mL) for 16 h. Workup as before provided **1** (176 mg, 81%) and TsCl (785 mg, 98%).

A similar experiment in which the TsNSO (1.08 mmol), $SOCl_2$ (5.5 mmol), naphthoquinone (0.42 mmol), and pyridine (12.5 mmol) in benzene (15 mL) were refluxed together for 2 h gave **1**, after flash chromatography in 64% yield.

Other Entries. The reactants were combined and refluxed, and the reaction mixtures were then worked up as in the procedure for entry 1. The stoichiometries are shown in Table 1, and the amounts of naphthoquinone used were 158 mg for all the experiments, with the following exceptions: the experiments in entries 13, 15, 17, and 18 used 80 mg; that in entry 12 used 65 mg, and that in entry 22 used 316 mg. Naphthoquinone was eluted by 10:1 CH_2Cl_2–hexane and TsCl by 2:3

(62) Barton and Bubb's conclusion,[7a] that "the multiplicity of pathways by which these reagents can react, although mechanistically fascinating, imposes limitations on their synthetic utility," although qualified, seems overly pessimistic.

(63) Villena-Blanco, M.; Jolly, W. L. *Inorg. Synth.* **1967**, *9*, 98.

(64) Alange, G. G.; Banister, A. J.; Bell, B. *J. Chem. Soc., Dalton Trans.* **1972**, 2399.

CH_2Cl_2–hexane. The solutions in the experiments in entries 15, 16, and 25–27 turned green and then red-brown.

Preparation of Thiadiazoles According to Table 2. The procedures were essentially those used for the experiment in Table 1, entry 1, and the stoichiometries and reaction times are those listed in Table 2. The following were prepared using the procedures cited: **7** (R = Me),[65,66] **9**,[67] 1,4-anthraquinone,[68] **13** (R = H),[69] **13** (R = $O(CH_2)_2OBu$),[70] and **15**.[71] Helicenequinone **17** was obtained from Willmore.[23] Helicenequinone **19** (X = O-decyl) was obtained from Liu.[72] Helicenequinone **19** [X = $O(CH_2)_2OBu$] was prepared following steps similar to those used to prepare **17**.[73]

Entry 2: yellow solid, mp 296 °C (lit.[2b] mp 293 °C). The spectroscopic data match those already published:[2b] ^1H NMR (200 MHz, $CDCl_3$) δ 7.94 (dd, J = 5.8, 3.3 Hz, 2 H), δ 8.48 (dd, J = 5.8, 3.3 Hz, 2 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 178.3, 159.8, 134.9, 134.1, 127.6; MS (EI) *m/e* (rel int) 264 (100), 158 (31), 104 (100), 76 (71); HRMS calcd for $C_{10}H_4N_2O_2Se$ 263.9439, found 263.9442.

Entry 3 (8, R = Me, X = S): yellow solid, mp 187–189 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.71 (dd, J = 8.0, 1.2 Hz, 1 H), 8.23 (d, J = 1.2 Hz, 1 H), 8.33 (d, J = 8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.5, 176.0, 156.4, 156.3, 147.0, 136.1, 133.6, 131.5, 128.8, 128.7, 21.9; MS (EI) *m/e* (rel int) 230 (41), 150 (29), 118 (100), 89 (20); HRMS calcd for $C_{11}H_6N_2O_2S$ 230.0150, found 230.0144.

Entry 4 (8, R = CN, X = S): yellow solid, mp 261.5–263 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 8.18 (dd, J = 8, 1.7 Hz, 1 H), 8.57 (d, J = 8 Hz, 1 H), 8.72 (d, J = 1.2 Hz, 1 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 175.7, 175.3, 156.5, 156.4, 137.9, 136.6, 134.5, 131.2, 128.2, 117.3, 116.9; MS (EI) *m/e* (rel int) 241 (28), 161 (59), 101 (26), 83 (100); HRMS calcd for $C_{11}H_3N_3O_2S$ 240.9946, found 240.9946.

Entry 6 (10): yellow solid, mp 199.5–201 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 9.05 (s, 1 H), 8.54 (dd, J = 8 Hz, 1.7 Hz, 1 H), 8.51 (d, J = 8 Hz, 1 H), 4.05 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 175.1, 165.0, 156.2, 156.1, 136.3, 136.2, 135.7, 133.8, 129.8, 128.9, 53.2; MS (EI) *m/e* (rel int) 274 (60), 243 (100), 229 (10), 215 (21), 187 (18), 103 (15), 75 (18); HRMS calcd for $C_{12}H_6N_2O_4S$ 274.0078, found 274.0059.

Entry 7 (12): pale yellow solid, mp 100–101 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 2.25 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 154.8, 145.5, 13.0; MS (EI) *m/e* (rel int) 194 (100), 84 (22), 64 (36), 53 (36); HRMS calcd for $C_8H_6N_2O_2S$ 194.0150, found 194.015.

Entry 8 (6): yellow solid, mp 290–291 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.81 (dd, J = 6.3, 3.3 Hz, 2 H), 8.18 (dd, J = 6.1, 3.3 Hz, 2 H), 9.02 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 157.6, 135.7, 131.9, 131.0, 130.9, 129.6; IR ($CHCl_3$, cm^{-1}) 3019, 1692 (s, CO), 1621, 1453, 1414, 1349 (m), 1013, 930; MS (EI) *m/e* (rel int) 266 (M^+, 65), 154 (50); HRMS calcd for $C_{14}H_6N_2O_2S$ 266.0150, found 266.0165.

Entry 9 (14, R = H, X = S): yellow solid, mp 195–196 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.73–7.78 (m, 1 H), 7.83–7.89 (m, 1 H), 7.99 (d, J = 8.2 Hz, 1 H), 8.34 (d, J = 8.5 Hz, 1 H), 8.50 (d, J = 8.8 Hz, 1 H), 9.78 (d, J = 8.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.2, 176.9, 157.1, 154.7, 137.2, 136.9, 134.8, 131.1, 130.9, 129.8, 129.5, 129.0, 128.5, 123.0; IR ($CHCl_3$, cm^{-1}) 3015, 1681 (s, CO), 1518, 1420, 1371, 930, 908; MS (EI, 200–250 °C) *m/e* (rel int) 266 (100), 238 (12), 186 (25), 154 (20), 126 (77); HRMS calcd for $C_{14}H_6N_2O_2S$ 226.0150, found 226.0149.

Entry 10 (14, R = $O(CH_2)_2OBu$, X = Se): orange solid, mp 193–195 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 0.95 (t, J = 6.5 Hz, 3 H), 1.45 (m, 2 H), 1.65 (m, 2 H), 3.73 (t, J = 6.5 Hz, 2 H), 4.01 (t, J = 6.5 Hz, 2 H), 4.55 (t, J = 6.5 Hz, 2 H), 7.63–7.89 (m, 3 H), 8.43 (d, J = 8 Hz, 1 H), 9.76 (d, J = 8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.2, 178.2, 160.9, 158.2, 137.2, 132.5, 131.4, 128.9, 128.7, 128.5, 123.4, 123.0, 101.3, 71.7, 69.0, 68.7, 31.9, 19.0, 13.8; MS (CI, NH_3) 431 (M^+ + 1), 448 (M^+ + 18); HRMS (FAB) calcd for $C_{20}H_{19}N_2O_4Se$ (MH^+) 431.0512, found 431.0539.

Entry 11 (16): red solid, mp 289–290 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.53 (td, J = 7.7, 1.4 Hz, 1 H), 7.67 (td, J = 7.4, 1.2 Hz, 1 H), 7.75 (d, J = 8.8 Hz, 1 H), 7.92 (dd, J = 7.8, 1.6 Hz, 1 H), 7.98 (d, J = 8.4 Hz, 1 H), 8.21 (d, J = 8.2 Hz, 1 H), 8.43 (d, J = 8.8 Hz, 1 H), 8.50 (d, J = 8.4 Hz, 1 H); MS (EI, 200–250 °C) *m/e* (rel int) 316 (26), 84 (20), 49 (100); HRMS calcd for $C_{18}H_8N_2O_2S$ 316.0306, found 316.0300. The solubility was too low for the ^{13}C NMR spectrum to be determined.

Entry 12. CH_2Cl_2–EtOAc (10:1) was the eluant: deep red solid, mp 165–166 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 8.56 (d, J = 8 Hz, 2H), 8.11 (d, J = 8 Hz, 2H), 7.83 (s, 2H), 4.52–4.76 (m, 4H), 4.07 (t, J = 6 Hz, 4H), 3.65 (t, J = 7 Hz, 4H), 1.60–1.75 (m, 4H), 1.40–1.55 (m, 4H), 0.92–1.02 (t, J = 7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.2, 175.4, 160.2, 156.6, 154.9, 135.8, 133.1, 132.4, 129.7, 129.4, 128.7, 126.7, 122.7, 103.3, 71.5, 69.3, 68.7, 31.7, 19.3, 13.9; MS (CI, NH_3) 736 (M^+), 737 (M^+ + 1), 754 (M^+ + 18); HRMS (FAB) calcd for $C_{38}H_{33}N_4O_8S_2$ (MH^+), 737.1740, found 737.1766.

Entry 13. CH_2Cl_2–EtOAc (1:1) was the eluant: deep red solid, mp 222–223 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 8.58 (d, J = 8 Hz, 2H), 8.13 (d, J = 8 Hz, 2H), 7.85 (s, 2H), 4.52–4.78 (m, 4H), 4.06 (t, J = 6 Hz, 4H), 3.65 (t, J = 7 Hz, 4H), 1.60–1.75 (m, 4H), 1.40–1.55 (m, 4H), 0.99 (t, J = 7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.2, 177.0, 160.2, 160.0, 158.5, 136.0, 133.0, 132.5, 129.9, 129.7, 128.8, 127.0, 122.8, 103.3, 71.9, 69.6, 68.9, 32.0, 19.8, 14.0; MS (FAB) 830 and 832 (M^+, ca. 1:1); HRMS (FAB) calcd for $C_{38}H_{33}N_4O_8Se_2$ (MH^+), 831.0649 and 833.0638 (ca.1:1), found 831.0632 and 833.0643 (ca.1:1).

Entry 14. CH_2Cl_2–EtOAc (10:1) was the eluent: orange solid, mp 227–230 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.48 (s, 2H), 7.85 (s, 2H), 4.52–4.68 (m, 4H), 4.02 (t, J = 6 Hz, 4H), 3.64 (t, J = 7 Hz, 4H), 1.60–1.70 (m, 4H), 1.38–1.50 (m, 4H), 0.96 (t, J = 7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.4, 176.4, 159.6, 156.9, 154.7, 134.6, 130.7, 129.6, 128.8, 123.4, 104.1, 71.4, 69.3, 68.6, 31.6, 19.2, 13.8; MS (CI, NH_3) 687 (M^+ + 1), 704 (M^+ + 18); HRMS (FAB) calcd for $C_{34}H_{31}N_4O_8S_2$ (MH^+), 687.1583, found 687.1601.

Entry 15. CH_2Cl_2–EtOAc (25:1) was the eluent: deep red solid, mp 159–161 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 8.50 (s, 2H), 7.83 (s, 2H), 4.35–4.55 (m, 4H), 1.95–2.12 (m, 4H), 1.1–1.7 (m, 36H), 0.88 (t, J = 7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) only 20 lines could be seen δ 177.8, 176.8, 160.0, 157.0, 155.0, 135.0, 131.0, 129.8, 129.1, 123.6, 104.0, 70.0, 32.0, 29.6 (two lines), 29.4, 29.0, 26.0, 23.0, 14.6; MS (FAB) 822 (M^+) and 823 (MH^+); HRMS (FAB) calcd for $C_{46}H_{55}N_4O_8S_2$ (MH^+) 823.3563, found 823.3560.

S_4N_4 + 2,3-Dichloronaphthoquinone. A solution of 2,3-dichloro-1,4-naphthoquinone (227 mg, 1 mmol), S_4N_4 (370 mg, 2 mmol), and pyridine (1 mL, 12.5 mmol) in benzene (25 mL) was refluxed for 24 h. Workup as above gave **1** (172 mg, 80%) and recovered S_4N_4 (151 mg, eluted with 1:1 CH_2Cl_2–petroleum ether). No reaction took place (TLC analysis) when the same experiment was performed without the pyridine.

Formation of Thiazoles Induced by 2,3-Dichloro-1,4-naphthoquinone. 1,4-Naphthoquinone + S_4N_4 (eq 11). A mixture of 2,3-dichloro-1,4-naphthoquinone (227 mg, 1 mmol), naphthoquinone (80 mg, 0.5 mmol), S_4N_4 (375 mg, 2.03 mmol), and pyridine (1 mL, 12.5 mmol) in benzene (25 mL) was refluxed for 24 h. Workup as above gave 300 mg of **1**, a 92% yield based on the sum of the 2,3-dichloro-1,4-naphthoquinone and naphthoquinone used. A similar experiment, using 1.5 g of 2,3-dichloro-1,4-naphthoquinone (6.6 mmol), 0.95 g of naphthoquinone (6.0 mmol), 1.4 g of S_4N_4 (7.6 mmol), and 1.5 mL of pyridine (18.5 mmol) in benzene (150 mL), gave 1.9 g of **1**, a 70% yield based on the sum of the 2,3-dichloro-1,4-naphthoquinone and naphthoquinone used.

(65) Fieser, L. F. *J. Am. Chem. Soc.* **1948**, *70*, 3165.
(66) Torres, E.; Panetta, C. A.; Heimer, N. E.; Clark, B. J.; Hussey, C. L. *J. Org. Chem.* **1991**, *56*, 3737.
(67) Akpuaka, M. U.; Beddoes, R. L.; Bruce, J. M.; Fitzjohn, S.; Mills, O. S. *J. Chem. Soc., Chem. Commun.* **1982**, 686.
(68) Gupta, D. N.; Hodge, P.; Khan, N. *J. Chem. Soc., Perkin Trans. 1* **1981**, 689.
(69) Manning, W. B.; Kelly, T. P.; Muschik, G. M. *J. Org. Chem.* **1980**, *45*, 2535.
(70) Willmore, N. D.; Hoic, D. A.; Katz, T. J. *J. Org. Chem.* **1994**, *59*, 1889.
(71) Davies, W.; Porter, Q. N. *J. Chem. Soc.* **1957**, 4967.
(72) Liu, L. Ph.D. Dissertation, Columbia University, 1991.
(73) Shi, S. Ph.D. Dissertation, Columbia University, 1994.

1,4-Anthraquinone + S_4N_4 (eq 12). A mixture of 2,3-dichloro-1,4-naphthoquinone (227 mg, 1 mmol), 1,4-anthraquinone (150 mg, 0.72 mmol), S_4N_4 (250 mg, 1.36 mmol), and pyridine (790 mg, 10 mmol) in benzene (25 mL) was refluxed for 30 h. Chromatography, using CH_2Cl_2–petroleum ether (10:1) as the eluant, gave **1** (192 mg, an 89% yield based on the 2,3-dichloro-1,4-naphthoquinone) and **6** (140 mg, a 73% yield based on the 1,4-anthraquinone).

Refluxing 1,4-anthraquinone (104 mg, 0.5 mmol), S_4N_4 (184 mg, 1.0 mmol), and pyridine (1 mL, 12.5 mmol)—but no 2,3-dichloro-1,4-naphthoquinone—in benzene (25 mL) for 24 h left only starting materials (TLC analysis).

1,4-Anthraquinone + Ethyl *N*-Sulfinylcarbamate. A mixture of 2,3-dichloro-1,4-naphthoquinone (227 mg, 1 mmol), 1,4-anthraquinone (150 mg, 0.72 mmol), ethyl *N*-sulfinylcarbamate (1.35 g, 10 mmol), and pyridine (2.2 mL, 27 mmol) in benzene (25 mL) was refluxed for 12 h. Chromatography, using CH_2Cl_2–petroleum ether (10:1) as the eluant, gave **1** (125 mg, a 58% yield based on the 2,3-dichloro-1,4-naphthoquinone) and recovered 1,4-anthraquinone (76 mg, 51%). None of compund **6** could be found.

Dichlorination of Naphthoquinone by $SOCl_2$. A solution of naphthoquinone (80 mg, 0.5 mmol), thionyl chloride (0.5 mL, 7 mmol), and pyridine (1.0 mL, 12.5 mmol) in benzene (25 mL) was refluxed for 3.5 h. No 2-chloro-1,4-naphthoquinone was detectable by TLC analysis. Chromatography, with CH_2Cl_2–hexane (1:1) as the eluant, gave 2,3-dichloro-1,4-naphthoquinone (**2**, 100 mg, 87% yield), identical to a commercially available sample.

On a scale in which the molar amounts of the reagents above were 10, 42, and 100 mmol, and the amount of benzene was 200 mL, the yield, after the solution was decanted from precipitate and worked as before, was 1.51 g (a 66% yield). A duplicate of the experiment, but with O_2 bubbling through the reaction mixture, gave 1.45 g (a 64% yield).

The other experiments in Table 3 were carried out using 25 mL of benzene and the following amounts of quinone or hydroquinone (in mg, source identified by a reference): entry 2, 192;[74] entry 3, 172;[66] entry 4, 100;[66] entry 5, 80;[75] entry 6, 90;[70] entry 7, 162;[71] entry 8, 1200;[75] entry 9, 95;[75] entry 10, 226.[76] The products were identified as follows.

Entry 2. TLC analysis identified 2-chloro-1,4-naphthoquinone in the reaction product of this and all repetitions of the experiment. 2,3-Dichloro-1,4-napthoquinone was isolated and identified as before.

Entry 3: yellow solid, mp 147–150 °C (lit.[79] mp 149–150 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.53 (s, 3H), 7.59 (d, J = 8 Hz, 1H), 7.98 (s, 1H), 8.08 (d, J = 8 Hz, 1H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.1, 175.8, 146.0, 143.5, 143.2, 135.3, 130.1, 128.6, 128.1, 127.9, 22.0; MS (EI) *m/e* (rel int) 242 (M^+, 10), 240 (M^+, 15), 205 (14), 177 (15), 114 (20), 94 (57), 89 (94), 87 (100); HRMS (EI) calcd for $C_{11}H_6Cl_2O_2$ 239.9745, 241.9717 (100:66), found 239.9742, 241.9729 (100:63).

Entry 4: pale yellow solid, mp 185–187 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.21 (d, J = 2 Hz, 1H), 8.20 (d, J = 8 Hz, 1H), 7.84 (dd, J = 8, 2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.7, 175.5, 144.5, 143.7, 143.6, 134.6, 131.3, 130.8, 128.3, 127.8, 44.2; MS (EI) *m/e* (rel int) 274 (M^+, 33), 276 (M^+, 26), 278 (M^+, 12), 239 (100), 211 (39), 183 (13), 148 (16), 113 (47), 87 (100); HRMS (EI) calcd for $C_{11}H_5Cl_3O_2$ 273.9355, 273.9327, 277.9299, found 273.9363, 275.9342, 277.9318.

Entry 6: red solid, mp 226–227 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.50 (d, J = 8 Hz, 1H), 8.3.5 (d, J = 8 Hz, 1H), 7.60–7.85 (m, 2H), 7.55 (s, 1H), 4.20 (s, 3H); no ^{13}C NMR was obtained due to poor solubility; MS (CI, CH_4) *m/e* 307 (M^+ + 1), 335 (M^+ + 29); HRMS (EI) calcd for $C_{15}H_8Cl_2O_3$ 305.9850, 307.9824 (3:2), found 305.9858, 307.9845 (3:2).

Entry 7: red solid, mp 109–110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, J = 8 Hz, 1H), 8.21 (d, J = 8 Hz, 1H), 7.65 (t, J = 8 Hz, 1H), 7.55 (t, J = 8 Hz, 1H), 4.38 (s, 2H), 3.96 (t, J = 6 Hz, 2H), 3.60 (t, J = 6 Hz, 2H), 1.65 (m, 2H), 1.45 (m, 2H), 0.97 (t, J = 8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 176.2, 160.0, 142.2, 139.7, 133.2, 131.6, 131.0, 128.3, 127.8, 127.4, 122.3, 119.1, 101.0, 71.3, 68.62, 68.58, 31.9, 19.2, 13.9; MS (EI) *m/e* 392 (M^+); HRMS (EI) calcd for $C_{20}H_{18}Cl_2O_4$ 392.0582, 394.0557, found 392.0584, 394.0583.

Entry 8. The ^{1}H NMR (200 MHz, $CDCl_3$) was identical to that of a sample from Aldrich Chemical Co., Inc.: δ 2.21 (s, 3H), 6.85 (s, 1H), 7.75 (m, 2H), 8.10 (m, 2H).

Entry 9. The ^{1}H NMR (200 MHz, $CDCl_3$) was identical to that of a sample prepared by a published procedure:[77] δ 3.93 (s, 3H), 6.19 (s, 1H), 7.75 (m, 2H), 8.12 (m, 2H).

Entry 10: mp 170–172 °C (lit.[76,78] mp 175, 173 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.53 (s, 3H), 7.59 (d, J = 8 Hz, 1H), 7.80 (m, 2H), 8.08 (s, 1H), 8.19 (d, J = 8 Hz, 1H), 8.30 (m, 2H); MS (EI) 223 (M^+ + 1), 222 (M^+); HRMS (EI) calcd for $C_{15}H_{10}O_2$ 222.0681, found 222.0676.

Chlorination of 1,4-Naphthoquinone by SCl_2. 1,4-Naphthoquinone (1.58 g, 10 mmol), sulfur dichloride (4 g, 80%, containing S_2Cl_2, ca. 31 mmol), and pyridine (1 g, 12.6 mmol) were refluxed in benzene (80 mL) for 1.5 h. After the benzene had been stripped, the residue was chromatographed. Elution with 1:1 CH_2Cl_2–petroleum ether gave 2-chloro-1,4-naphthoquinone (1.37 g, 71%): a yellow solid, mp 107–109 °C (lit.[79] mp 109.5–112.5 °C, lit.[80] mp 117 °C); its ^{1}H NMR spectrum (200 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.80 (m, 2H), 8.10 (m, 1H), 8.20 (m, 1H) is similar to that reported (δ 7.20, 7.76, and 8.12);[80] MS (EI) 192 (M^+)/194 (M^+) = 100/34; HRMS (EI) calcd for $C_{10}H_5ClO_2$ 191.9978, 193.9951 (100:33.6), found 191.9967, 193.9951 (100:33).

Oxidation of 2-Methoxy-1,4-dihydroxynaphthalene by $SOCl_2$. 2-Methoxy 1,4-dihydroxynaphthalene (95 mg, 0.5 mmol), $SOCl_2$ (300 m g, 2.52 mmol), and pyridine (1 mL, 12.5 mmol) in benzene (25 mL) were refluxed for 2 h. After benzene had been removed, the residue was chromatographed. Elution with CH_2Cl_2 gave 2-methoxy-1,4-naphthoquinone (82 mg, 87%), identified by comparing its ^{1}H NMR spectrum (200 MHz, $CDCl_3$) with that of a sample prepared by a published procedure:[77] δ 3.93 (s, 3H), 6.19 (s, 1H), 7.75 (m, 2H), 8.12 (m, 2H).

Chlorination of 2-Methoxy-1,4-naphthoquinone by SCl_2. 2-Methoxy-1,4-naphthoquinone[77] (188 mg, 1 mmol), SCl_2 (0.4 mL, 80%, containing S_2Cl_2, ca. 5 mmol), and pyridine (1 mL, 12.5 mmol) was refluxed in benzene (25 mL) for 0.5 h. After benzene had been stripped, chromatography, with CH_2Cl_2–hexane (3:1) as the eluant, gave 2-methoxy-1,4-naphthoquinone (102 mg, 46%): a yellow solid, mp 144–146 °C (lit.[81] mp 145–146 °C); its ^{1}H NMR spectrum (200 MHz, $CDCl_3$) was identical with that of a sample prepared by a known procedure[81] δ 7.75 (m, 2H), 8.13 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.5, 178.2, 134.2, 133.8, 130.9, 130.6, 128.1, 128.1, 126.8, 126.7, 61.6; MS (EI) *m/e* (rel int) 224 (36), 222 (100), 157 (59), 129 (35), 123 (92), 104 (24), 84 (16); HRMS (EI) calcd for $C_{11}H_7O_3Cl$ 222.0084, 224.0058, found 222.0084, 224.0046.

Oxidation of 1,4-Dihydroxynaphthalene in the Absence of Pyridine by Either $SOCl_2$ or by TsNSO. 1,4-Dihydroxynaphthalene (1.60 g, 10 mmol) and $SOCl_2$ (2.4 g, 20 mmol) in benzene (80 mL) were refluxed for 2 h. Chromatography, eluting with CH_2Cl_2, gave 1,4-naphthoquinone (1.45 g, 92%), identified by its ^{1}H NMR (200 MHz, $CDCl_3$) spectrum. In another experiment, 160 mg of 1,4-dihydroxynaphthalene (1 mmol) and 1 mL of $SOCl_2$ (14 mmol), after refluxing for 3.5 h in 25 mL of benzene, gave 141 mg of 1,4-naphthoquinone (89% yield). Similarly, 1,4-dihydroxynaphthalene (100 mg,

(74) Prepared as described in the Experimental Section.
(75) The quinone was reduced with zinc in acetic acid according to the procedure of ref 66.
(76) Diels, O.; Alder, K. *Chem. Ber.* **1929**, *62*, 2337. (b) The material was prepared following ref 65, with glacial acetic acid as the solvent. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.7 (s, 3H), 2.2 (m, 2H), 2.5 (m, 2H), 3.4 (m, 2H), 5.4 (m, 1H), 7.75 (m, 2H), 8.05 (m, 2H).
(77) Otsuki, T. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 3089.
(78) Fieser, L. F. *Organic Syntheses*; Wiley: New York, 1932; Collect. Vol. I, p 353.
(79) Gaertner, R. *J. Am. Chem. Soc.* **1954**, *76*, 6150.
(80) Cameron, D. W.; Feutrill, G. I.; Patti, A. F. *Aust. J. Chem.* **1979**, *32*, 575.
(81) Hodnett, E. M.; Wongwiechintana, C.; Dunn, W. J., III; Marrs, P. *J. Med. Chem.* **1983**, *26*, 570.

0.625 mmol) and TsNSO (260 mg, 1.2 mmol) in benzene (20 mL) after refluxing for 1 h gave 80 mg (81%) of 1,4-naphthoquinone.

2,3-Dichloro-1,4-naphthoquinone + Methyl *N*-Sulfinylcarbamate. Methyl *N*-sulfinylcarbamate (530 mg, 4.4 mmol), pyridine (1 mL, 12.5 mmol), and 2,3-dichloro-1,4-naphthoquinone (227 mg, 1 mmol) in benzene (25 mL) was refluxed for 12 h, Chromatography gave 131 mg of **1** (61% yield). If a similar reaction was stopped after 4 h, impure **1** was isolated in tiny amount (10 mg, <5%), and 70 mg (31%) of the 2,3-dichloro-1,4-naphthoquinone was recovered.

The same experiment, but without pyridine, gave no **1** after 12 h of reflux, and TLC analysis indicated that most of the 2,3-dichloro-1,4-naphthoquinone remained.

Synthesis of 25. Chloranil + S_4N_4. Chloranil (492 mg, 2 mmol), S_4N_4 (736 mg, 4 mmol), and pyridine (2 mL, 25 mmol) in benzene (25 mL) was refluxed for 24 h. The precipitate filtered from the cooled mixture was washed with water, dried in the air, and recrystallized from DMF. The properties of the resulting pale brown plates (231 mg, 51% yield, mp > 300 °C) match those reported:[2b] mp > 300 °C; ^{13}C NMR (75 MHz, DMSO-d_6) 168.8, 157.9; IR (KBr, cm^{-1}) 1706 (C=O), 1450 (C=N); ^{1}H (EI) *m/e* (rel int) 224 (100), 196 (54), 166 (8), 138 (5), 112 (17); HRMS (EI) calcd for $C_6N_4O_2S_2$ for 223.9463, found 223.9466.

Reaction of Methyl *N*-Sulfinylcarbamate with $SOCl_2$ and Pyridine. A mixture of methyl *N*-sulfinylcarbamate (1.21g, containing ca. 8% methyl carbamate, ca. 10 mmol), thionyl chloride (1.19 g, 10 mmol), and anhydrous pyridine (160 mg, 2 mmol) was stirred in a dried 25 mL round-bottomed flask, connected to a water condenser and $CaSO_4$ drying tube, and heated for 1.5–2 h in an oil bath at 70–80 °C. The color turned from colorless to yellow, to red, and finally to brown-yellow, gases evolved, and a mixture of a brown-yellow solid and some liquid remained. Benzene (10 mL) was used to wash the liquid to the bottom of the flask and then was stripped. Drying at a pressure of 0.5 mmHg left 0.64 g of brown-yellow solid that did not dissolve in carbon tetrachloride, benzene, methylene chloride, and chloroform, but did in DMSO (giving a solution that turned from orange to red and, after 12 h, colorless, implying that a reaction occurs).

The yellow-brown solid prepared here and in repeated experiments had the following properties. It dissolved in ice–water and like S_4N_3Cl[8] reacted with KI in ice–water to form a brick-red solid, which turned black on standing.

When 520 mg of the yellow-brown solid was refluxed for 16 h with pyridine (2 mL) and naphthoquinone (158 mg, 1 mmol) in benzene (25 mL), **1** was obtained in 38% yield (83 mg).

When the yellow-brown solid was stirred with liquid ammonia (25 mL), cooled in a dry ice–acetone bath, for 2.5 h and then overnight at room temperature and the ammonia was evaporated, a brown solid remained, from which S_4N_4 (330 mg, identified by TLC and mass spectrometric analyses) was extracted with methylene chloride.

When the yellow-brown solid was refluxed in benzene for 1 h, S_4N_4 (180 mg) was isolated from the solution. Most of the solid did not dissolve. After having been pumped dry (0.5 mmHg) overnight, an insoluble yellow solid was obtained (480 mg). When heated for 2 h at 80–90 °C at a pressure of 0.6 mmHg, a white solid sublimed to the top of the flask and a bright yellow solid remained at the bottom, mp 180–200 °C dec after contracting at 120 °C. The yellow solid was identified by its IR spectra to be S_4N_3Cl + NH_4Cl. The IR spectrum in KBr (cm^{-1}): *3131, 2024, 1752, 1405*, 1191, **1161, ca. 1127, 998**, 766, **679, 602, 562, 466, 449**. The far IR spectrum in Nujol on a polystyrene film (cm^{-1}): **469, 453, 329, 249, 210, 173, 162**. The peaks identified in bold identify S_4N_3Cl,[15] those in italics identify NH_4Cl,[16] and the others are unassigned.

The white solid was identified as $(CH_3OCO)_2N^-$ (H-pyridine)$^+$ by the following data: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.86 (d, J = 6 Hz, 2 H, H2 of pyH^+), 8.48 (t, J = 8 Hz, 1 H, H4 of pyH^+), 8.00 (t, J = 7.5 Hz, 2 H, H3 of pyH^+), 7.16 (broad s, 1 H, NH), 3.80 (s, 6H, CH_3);[82] IR (KBr) 1794 cm^{-1};[83] MS *m/e* (rel int) 80 (100, pyH^+), 213 (32, M + 1). Washing with aqueous HCl and extraction into CH_2Cl_2 gave $(CH_3OCO)_2NH$, identified by the following: mp 120–130 °C (lit.[14] mp 128–130, 127–129 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.1 (broad s, 1 H), 3.73 (s, 6 H) [lit.[14a] ^{1}H NMR δ 7.35, 3.79, lit.[14b] ^{1}H NMR 10.5, 3.72]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.2, 151.3 [lit.[14a] ^{13}C NMR 53.0, 151.9]; MS (NH_3-CI) *m/e* 134 (M + 1), 151 (M + 18); MS (EI) *m/e* (rel int) 59 (100), 75 (12), 102 (72), 103 (80), 133 (4), 134 (5) [lit.[14b] MS 59 (100), 75 (19), 102 (54), 103 (60), 133 (2.5)].

Reaction of *N*-Sulfinyl-*p*-toluenesulfonamide with $SOCl_2$ and Pyridine. Similarly, 2.17 g of TsNSO (10 mmol) was combined with 1.19 g of $SOCl_2$ (10 mmol) and 160 mg of pyridine (2 mmol). After 2 h at ca. 80 °C, the product was refluxed with benzene and the resulting hot mixture filtered. The precipitate was pumped dry at 80 °C, giving 140 mg (20% based on nitrogen) of S_4N_3Cl, identified by its IR spectrum.

Preparation of Betaine 26. Naphthoquinone (1.58 g, 10 mmol), TsNSO (5.5 g, 25 mmol), and pyridine (3 mL, 38 mmol) were refluxed in benzene (60 mL) for 2 h. The hot mixture was filtered, and the red solid was washed with benzene, giving **26** (3.5 g, 87%): a red solid, mp 245–247 °C (lit.[30] mp 250 °C); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.00 (d, J = 6.4 Hz, 2H), 8.64 (t, J = 6.7 Hz, 1H), 8.17 (t, J = 6.7 Hz, 2H), 8.01 (d, J = 7.3 Hz, 2H), 7.87 (t, J = 7.3 Hz, 1H), 7.79 (t, J = 7.5 Hz, 1H), 7.48 (d, J = 7.3 Hz, 2H), 7.17 (d, J = 7.5 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 178.6, 172.2, 147.4, 146.5, 144.0, 141.8, 138.1, 132.6, 130.7, 129.9, 129.3, 126.5, 125.2, 124.6, 123.5, 123.2, 122.1, 19.0; MS (CI, CH_4) 405 (M^+ + 1), 433 (M^+ + 29); HRMS (FAB) calcd for $C_{22}H_{17}O_4S$ (MH^+) 405.0909, found 405.0918; IR 1694 cm^{-1}.[84]

TsNSNTs (740 mg, 2 mmol), naphthoquinone (158 mg, 1 mmol), and pyridine (1 mL, 12.5 mmol) in benzene (25 mL) when refluxed for 2 h similarly gave **26** (291 mg, 72%).

The product is identical with a sample prepared[30] by refluxing 2,3-dichloro-1,4-naphthoquinone (227 mg, 1 mmol), 4-toluenesulfonamide ($TsNH_2$, 171 mg, 1 mmol), and pyridine (1 mL, 12.5 mmol) in benzene (25 mL) for 2 h. Extraction with CH_2Cl_2 (200 mL), washing with NaOH (1 N) and then with water, drying, and stripping the solvent gave 250 mg (62%) of **26**.

Refluxing 2,3-dichloro-1,4-naphthoquinone (100 mg, 0.44 mmol), TsNSO (600 mg, 2.76 mmol), and pyridine (1 mL, 12.5 mmol) in benzene (25 mL) for 3 h gave 128 mg of **26** (72%). Similarly, 2,3-dichloro-1,4-naphthoquinone (227 mg, 1 mmol), TsNSNTs (420 mg, 1.14 mmol), and pyridine (200 mg, 12.5 mmol) in benzene (25 mL) when refluxed for 2 h gave 306 mg of **26** (75%).

Preparation of the Betaine from 1,4-Anthraquinone. Refluxing 1,4-anthraquinone (1 g, 4.8 mmol, prepared according to ref 68), TsNSO (2.5 g, 11.5 mmol), and pyridine (2 mL, 25 mmol) in benzene (60 mL) for 3 h gave the betaine (1.7 g, 78%). Decreasing the amount of TsNSO to 1.5 g (6.9 mmol) decreased the yield to 0.8 g (37%): yellow solid, mp 264–265 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 9.04 (d, J = 5.6 Hz, 2H), 8.61–8.67 (m, 3H), 8.16–8.32 (m, 4H), 7.73–7.77 (m, 2H), 7.49 (d, J = 8 Hz, 2H), 7.18 (d, J = 8 Hz, 2H), 2.30 (s, 3H); MS (CI, CH_4) *m/e* (rel int) 483 (M^+ + 29, 8), 455 (M^+ + 1, 48), 327 (15), 299 (100), 279 (82); HRMS (FAB) calcd for $C_{26}H_{19}N_2O_4S$ (MH^+) 455.1066, found 455.1072. It was too insoluble for the ^{13}C NMR spectrum to be measured.

Preparation of the Betaine from 1,4-Phenanthraquinone. Refluxing 1,4-phenanthraquinone (60 mg, 0.288 mmol, prepared according to refs 69 and 70), TsNSO (370 mg, 1.7 mmol), and pyridine (0.5 mL, 6.25 mmol) in benzene (25 mL) for 2 h gave the betaine (84 mg, 64%): a purple solid, mp 264–265 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.66 (m, 1H), 9.05 (d, J = 6.4 Hz, 2H), 8.68 (t, J = 7.6 Hz, 1H), 8.31 (d, J = 7.8 Hz, 1H), 8.21 (t, J = 7.3 Hz, 2H), 8.07 (d, J = 8 Hz, 2H), 7.70 (m, 2H), 7.52 (d, 7.6 Hz, 2H), 7.19 (d, J = 7.6 Hz, 2H), 2.30 (s,

(82) PyD$^+$DSO$_4^-$ in D_2O: δ 8.85, 8.70, 8.13: *Handbook of Proton-NMR Spectra and Data*; Asahi Research Center Co., Ltd., Ed.; Academic Press, Inc.: New York, 1986; Vol. 6, p 108, spectrum 4211.

(83) The picrate of 1-((ethoxycarbonyl)imino)-2-methylpyridinium ylide shows $\nu_{C=O}^{KBr}$ 1750 cm^{-1}: Sasaki, T.; Kanematsu, K.; Kakehi, A.; Ichikawa, I.; Hayakawa, K. *J. Org. Chem.* **1970**, *35*, 426.

(84) The *p*-nitrophenyl analogue (**28**) exhibits resonances of the naphthalene and pyridine protons at δ 8.97, 8.52, and 8.18–7.64 and an IR maximum at 1680 cm^{-1}.[33]

3H); MS (CI, CH_4) 455 ($M^+ + 1$), 383 ($M^+ + 29$); HRMS (FAB) calcd for $C_{26}H_{19}N_2O_4S$ (MH^+) 455.1066, found 455.1069. It was too insoluble for the ^{13}C NMR spectrum to be measured.

Conversion of 26 into 1. Betaine **26** (404 mg, 1 mmol), thionyl chloride (0.6 g, 5 mmol), ethyl *N*-sulfinylcarbamate (650 mg, 4.8 mmol), and pyridine (1 mL, 12.5 mmol) in benzene (25 mL) were refluxed for 2 h. Chromatography, eluting with CH_2Cl_2–petroleum ether (2:3), gave TsCl (88 mg, 46%). Further elution with CH_2Cl_2 gave **1** (148 mg, 68%).

A mixture of naphthoquinone (158 mg, 1 mmol), TsNSO (1.12 g, 5.2 mmol), and pyridine (1 mL, 12.5 mmol) in benzene (25 mL) was refluxed for 30 min. A large amount of red solid formed. $SOCl_2$ (1 g, 8.4 mmol) was added to the mixture, and refluxing was continued for 2 h. The red solid disappeared and a red-brown solution formed. Chromatography, eluting with CH_2Cl_2, gave 115 mg (53%) of **1**.

When **26** (100 mg) and $SOCl_2$ (1 g) were refluxed for 12 min in 20 mL of benzene, no **1** formed (TLC analysis).

Preparation of 2-Amino-3-(*p*-toluenesulfonamido)-1,4-naphthoquinone (27). Naphthoquinone (158 mg, 1 mmol), TsNSO (560 mg, 2.6 mmol), and pyridine (0.5 mL, 6.25 mmol) in benzene (25 mL) were refluxed for 2 h. Large amounts of red solid formed. Pyrrolidine (1 mL, excess) was added to the mixture, and refluxing was continued for 1 h. The red solid disappeared, and the solution turned brown. After the solvent had been stripped, chromatography, eluting with CH_2Cl_2–EtOAc (50:1), gave **27** (246 mg, 72%): an orange-red cotton-like solid, mp 210–211 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 7.4, 1.6 Hz, 1H), 7.86 (dd, J = 7.4, 1.6 Hz, 1H), 7.72 (d, J = 8 Hz, 2H), 7.58–7.66 (m, 2H), 7.22 (d, J = 8 Hz, 2H), 6.94 (s, 1H, D_2O exchangeable), 6.58 (bs, 2H, D_2O exchangeable), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.9, 177.9, 144.4, 142.5, 134.7, 134.3, 132.7, 131.3, 130.1, 129.6, 127.5, 126.5, 126.3, 111.6, 21.6; MS (CI, CH_4) 343 ($M^+ + 1$), 361 ($M^+ + 29$), 187 ($M^+ - 155$); HRMS (EI) calcd for $C_{19}H_{14}N_2O_4S$ 342.0674, found 342.0666.

Preparation of 2-Amino-3-(*p*-toluenesulfonamido)-1,4-anthraquinone. 1,4-Anthraquinone (208 mg, 1 mmol), TsNSO (760 mg, 3.5 mmol), and pyridine (2 mL, 25 mmol) in benzene (25 mL) were refluxed for 4 h. Pyrrolidine (1 mL, excess) was then added to the mixture, and refluxing was continued for 2.5 h. Workup as above and chromatography, with CH_2Cl_2 as the eluant, gave 2-amino-3-(*p*-toluenesulfonamido)-1,4-anthraquinone (205 mg, 52%), an orange cotton-like solid: mp 254–255 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.37 (s, 1H), 7.99 (m, 1H), 7.94 (m, 1H), 7.74 (d, J = 8 Hz, 2H), 7.61–7.67 (m, 2H), 7.20 (d, J = 8 Hz, 2H), 7.13 (s, 1H), 6.45 (bs, 2H), 2.32 (s, 3H); MS (EI) *m/e* (rel int) 392 (48), 237 (68), 210 (100), 183 (21), 171 (36), 155 (31), 127 (29), 107 (19); HRMS (EI) calcd for $C_{21}H_{16}N_2O_4S$ 392.0831, found 392.0840. It was too insoluble for the ^{13}C NMR spectrum to be determined.

Preparation of 2-Amino-3-(*p*-toluenesulfonamido)-1,4-phenanthraquinone or 3-Amino-2-(*p*-toluenesulfonamido)-1,4-phenanthraquinone. 1,4-Phenanthraquinone (208 mg, 1 mmol), TsNSO (700 mg, 3.2 mmol), and pyridine (1 mL, 12.5 mmol) in benzene (25 mL) was refluxed for 2 h. Pyrrolidine (1 mL, excess) was then added, and refluxing was continued for 1 h. Workup as above and chromatography, with CH_2Cl_2–EtOAc (50:1) as the eluant, gave the amino(*p*-toluenesulfonamido)-1,4-phenanthraquinone (130 mg, 33%): a purple solid, mp 233–236 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.49 (d, J = 8 Hz, 1H), 8.10 (d, J = 8 Hz, 1H), 7.99 (d, J = 8 Hz, 1H), 7.85 (d, J = 7.5 Hz, 1H), 7.74 (d, J = 8 Hz, 1H), 7.71–7.75 (m, 1H), 7.61 (m, 1H), 7.20 (d, J = 8 Hz, 2H), 6.87 (s, 1H), 6.44 (bs, 2H), 2.34 (s, 3H); MS (CI, CH_4) 393 ($M^+ + 1$), 421 ($M^+ + 29$); HRMS (FAB) calcd for $C_{21}H_{17}N_2O_4S$ (MH^+) 393.0909, found 393.0916. It was too insoluble for its ^{13}C NMR spectrum to be determined.

Acknowledgment. We thank the National Science Foundation for its support and Mr. Luis Avila for helping us to determine far IR spectra.

JO941941V