Fraction 7 was successfully crystallized in the collection tube, leading to one crop of crystals, m.p. 90–93.5°, easily shown to be identical with an authentic sample of 2,3,4-trimethylquinoline, lit.[5] m.p. 90–92°, by the identity of their infrared spectra. A second crop, m.p. 67–75°, isolated in very small yield, was shown by mass spectra (parent peak at mass 171 ± 4) and ultraviolet spectra (long wave-length maxima at 320, 314, and 307 mμ) to be a trimethylquinoline. The infrared spectrum showed that substitution had occurred in the benzene ring (absorption at 775 and 820 cm.$^{-1}$) and in fact the spectrum proved to be identical with that of an authentic sample of 2,4,5-trimethylquinoline.[16]

"Butanone Anil" 2,4-Diethyl-2-methyl-1,2-dihydroquinoline.—Aniline and 2-butanone reacted according to the procedure given by Vaughan[4] for the preparation of 2,2,4-trimethyl-1,2-dihydroquinoline. 2-Butanone (835 g.) was passed into the reaction mixture of aniline (279 g.) and iodine, (9 g.), which was maintained at 170–175°. The product was crudely distilled to separate butanone and the bulk of the aniline, then fractionated on a 4-ft. glass helix column and the fraction, b.p. 170–174° (28 mm.), 95 g. (lit.[18] b.p. 152–153° at 12 mm.), collected. The n.m.r. showed a vinyl resonance at 4.95 τ, the NH resonance at 6.73 τ, and a quartet centered at 7.55 τ (J = 7.5 c.p.s.), assigned to the methylene group at position 4 of XII. The remainder of the spectrum consisted of the usual aromatic multiplet, a single resonance at 8.82 τ assigned to the methylene group at C-2 of XII, and a pattern of seven lines interpreted as a triplet centered at 8.87τ (J = 7.5 c.p.s.) overlapped on the low field side by a quartet centered at 8.69 τ (J = 7.5 c.p.s.) and on the high field side by a triplet centered at 9.13 τ (J = 7.5 c.p.s.). The seven line pattern thus represents the two methyl groups attached to methylenes at C-2 and C-4, and the methylene attached to the saturated center at C-2.

A sample purified by v.p.c. gave the following analysis.

Anal. Calcd. for $C_{14}H_{19}N$: C, 83.54; H, 9.49. Found: C, 83.53, 83.43; H, 9.17, 9.04.

(18) E. Knoevenagel, *Ber.*, **54**, 1728 (1921).

The hydrochloride of XII, heated for 5 min. at 285°, gave a mixture of quinolines which was analyzed on the previously described v.p.c. column. Six peaks were resolved, one representing *ca.* 50% of the quinoline product. N.m.r. analysis of this peak showed it to be 2-methyl-4-ethylquinoline. (The single methyl resonance occurs at 7.38 τ while the ethyl group gives a quartet at 7.03 τ and a triplet at 8.67 τ).

Anal. Calcd. for $C_{12}H_{13}N$: C, 84.16; H, 7.65; Found: C, 84.23, 84.12; H, 7.75, 7.62.

Base-Catalyzed Decomposition of XII.—The procedure of Vaughan[4] was used on a 1/10 scale. XII (0.2 mole, 40.4 g.) refluxed with sodium anilide for 3 hr. V.p.c. analysis of the products showed one major (more than 90%) component. N.m.r. analysis of the product confirmed its structure as 2,4-diethylquinoline. (A triplet representing the six methyl hydrogens falls at 8.63 τ while the two methylene quartets at 7.13 and 7.02 τ overlap to give a five-line pattern.)

Anal. Calcd. for $C_{13}H_{15}N$: C, 84.28; H, 8.16. Found: C, 84.51, 84.27; H, 8.15, 8.20.

2,4,8-Trimethylquinoline (V).—"Acetone *o*-toluidyl," 2,2,4,8-tetramethyl-1,2-dihydroquinoline was prepared by the method of Vaughan[4] for "acetone anil." *o*-Toluidine (1.5 moles, 170 g.) and acetone (500 ml.) yielded 33 g., b.p. 149–154° (30 mm.), lit.[18] b.p. 138.5–139.5° (14 mm.).

Anal. Calcd. for $C_{13}H_{17}N$: C, 83.36; H, 9.16. Found: C, 83.45, 83.29; H, 9.22, 9.04.

"Acetone *o*-toluidyl" (20 g.) was added to the mixture obtained by heating sodium (0.25 g.), *o*-toluidine (3.4 g.), and 0.5 g. of copper powder. The mixture was refluxed for 5 hr., then fractionated with a small Vigreux column, yielding a fraction of 3.46 g. of crude quinoline. Refractionation yielded crystalline V, b.p. 112–114° (3.0 mm.), m.p. 38.7–41.3°, lit.[15] m.p. 42°.

Acknowledgment.—This work was supported by a grant from the National Science Foundation.

The Chemistry of Thioether-Substituted Hydroquinones and Quinones. I. The 1,4-Addition of a Heterocyclic Mercaptan to Quinones

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Cyclopentadiene, 1,3-cyclohexadiene, and 2,3-dimethylbutadiene have undergone Diels–Alder addition to a variety of *p*-benzoquinones. The adducts were rearranged to the hydroquinone derivatives and then oxidized to their respective quinones. These quinones undergo normal 1,4-addition of a mercaptan. A new method of rearrangement of the quinone–cyclopentadiene adducts to their hydroquinone forms with triethylamine is reported. The 1,4-addition of a mercaptan to several *o*- and *p*-benzoquinones also is reported.

Many examples of 1,4-additions to quinones are in the literature which include the Thiele acylation reaction,[2,3] the addition of hydrogen halides,[4] of amines,[5] and mercaptans.[6]

The present paper concerns the addition of a heterocyclic mercaptan to unsubstituted, di-, and trisubstituted 1,4-quinones. The succeeding paper[7] concerns the mercaptan addition to monosubstituted 1,4-quinones.

The mercaptan used in this investigation was 1-phenyl-5-mercaptotetrazole[8] (hereafter called HPMT, **1**). The substance is an odorless, high-melting solid which is very acidic, a desirable property in ionic addition reactions to unsaturated compounds.[9] The mechanism of this 1,4-addition is unknown, but whether initial attack is by hydrogen ion, mercaptide ion, or the nucleophilic sulfur atom, the predicted products are the same. Steric effects may influence the course and rate of this reaction.

Addition reactions employing unsubstituted, disubstituted, or trisubstituted quinones normally give good yields of a single product. Contrary to previous reports,[5,9,10] no difficulty was encountered in controlling the reaction in order to obtain the monoaddition product with this mercaptan.

(1) Polaroid Corp., Cambridge 39, Mass.

(2) J. Thiele, *Ber.*, **31**, 1247 (1898).

(3) (a) H. G. H. Erdtman, *Proc. Roy. Soc.* (London), **A143**, 177 (1933–1934); (b) H. G. H. Erdtman and A. Léon, *Anales soc. españ. fis. quim.*, **32**, 614 (1934).

(4) J. Cason, R. E. Harman, S. Goodwin, and C. F. Allen, *J. Org. Chem.*, **15**, 860 (1950).

(5) H. Suida and W. Suida, *Ann.*, **416**, 113 (1918).

(6) J. M. Snell and A. Weissberger, *J. Am. Chem. Soc.*, **61**, 450 (1939).

(7) H. S. Wilgus, III, E. Frauenglass, E. T. Jones, R. F. Porter, and J. W. Gates, Jr., *J. Org. Chem.*, **29**, 594 (1964).

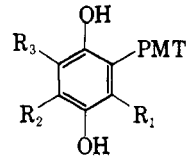
(8) M. Freund and H. Hempel, *Ber.*, **28**, 74 (1895).

(9) J. I. Cunneen, *J. Chem. Soc.*, 36, 134 (1947).

(10) A. Blackhall and R. H. Thomson, *ibid.*, 1138 (1953).

TABLE I

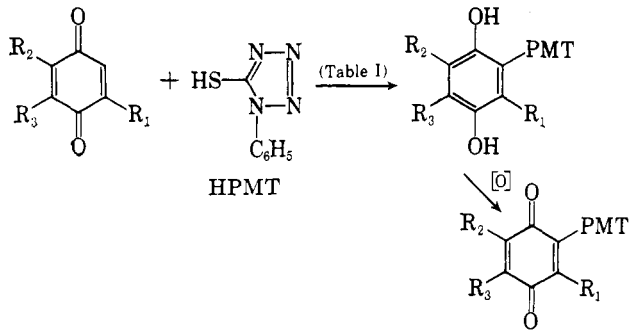
SUBSTITUTED HYDROQUINONES



R_1	R_2	R_3	Yield, %	M.p. dec., °C. (crystn. solvent)	Analysis, %	Calcd.	Found
H	H	H	94[a]	216–217 (acetone)	C	54.5	54.9
					H	3.5	3.8
					N	19.6	20.0
					S	11.2	11.2
CH_3	H	CH_3	60[b]	213–214 (acetone–chloroform)	C	57.3	57.1
					H	4.5	4.5
					N	17.8	18.1
					S	10.4	10.0
H	CH_3	CH_3	30[b]	155–157 (benzene–methanol)	C	57.3	57.1
					H	4.5	4.7
					N	17.8	18.1
					S	10.4	10.2
CH_3	CH_3	H	40[b]	188–189 (benzene–ethanol)	C	57.3	57.0
					H	4.5	4.3
					N	17.8	18.2
CH_3	CH_3	CH_3	54[b]	184–186 (acetone–methanol)	C	58.5	58.4
					H	4.9	4.9
					N	17.0	16.7

[a] For 3 hr. at room temperature in methanol. [b] Refluxed for 18 hr. in methanol.

The 1,4-addition products to the symmetrical quinones and to those quinones in which the structure of the product is unambiguous are listed in Table I. Addition to 2,5-di-*t*-butylquinone did not occur, illustrating the steric effect. All of the materials were prepared as indicated.



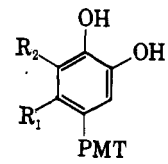
The addition of this mercaptan (**1**) to three *o*-quinones was accomplished in a similar manner, and the expected products were obtained. To our knowledge, these are the first reported 1,4-additions of a mercaptan to *o*-quinones. The materials are listed in Table II.

It has long been known that dienes will add to quinones.[11,12] The addition of 2,3-dimethylbutadiene, cyclopentadiene, and 1,3-cyclohexadiene to 2-(1′-phenyl-5′-tetrazolylthio)-1,4-benzoquinone (**3**), prepared by oxidation of hydroquinone **2** (Table I), proceeded smoothly in high yield. The 2,3-dimethylbutadiene and 1,3-cyclohexadiene adducts (**4** and **5**) rearranged readily with mineral acid[11] to produce the hydroquinones (**7** and **8**) as expected. Oxidation of these hydroquinones then produced the desired quinones (**10** and **11**). Addition of HPMT (**1**) to these quinones gave the hydroquinone derivatives (**13** and **14**). The cyclopentadiene adduct (**6**) did not rearrange with acid, probably owing to the strain imposed by this structure; its rearrangement is discussed later. The infrared spectra of adducts **4**, **5**, and **6** are consistent with the given structures.

This reaction sequence is illustrated in Tables III–VI. The diene adducts, 4a,5,8,8a-tetrahydro-1,4-naphthoquinones, are listed in Table III; the rearranged adducts, 5,8-dihydronaphthohydroquinones, in Table IV; the 5,8-dihydronaphthoquinones in Table V; and the substituted mercaptan–quinone adducts in Table VI.

TABLE II

SUBSTITUTED CATECHOLS



R_1	R_2	Yield, %	M.p. dec., °C. (crystn. solvent)	Analysis, %	Calcd.	Found
t-C_4H_9	H	54[a]	182–183 (acetone–chloroform)	C	59.6	59.6
				H	5.3	5.5
C_6H_5	H	35[b]	175–176 (acetone–chloroform)	C	63.0	62.6
				H	3.9	4.0
R_1,R_2= 		25[a]	183 (acetone–chloroform)	C	60.7	61.0
				H	3.6	4.0

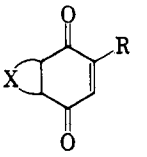
[a] Refluxed for 18 hr. in chloroform. [b] Refluxed for 72 hr. in chloroform.

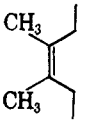
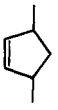
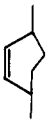
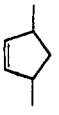
(11) O. Diels and K. Alder, *Ber.*, **62**, 2337 (1929).

(12) L. W. Butz and A. W. Rytina, "Organic Reactions," Coll. Vol. V, R. Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 136.

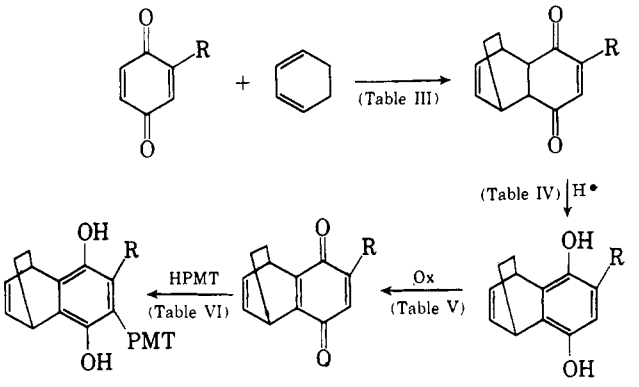
TABLE III

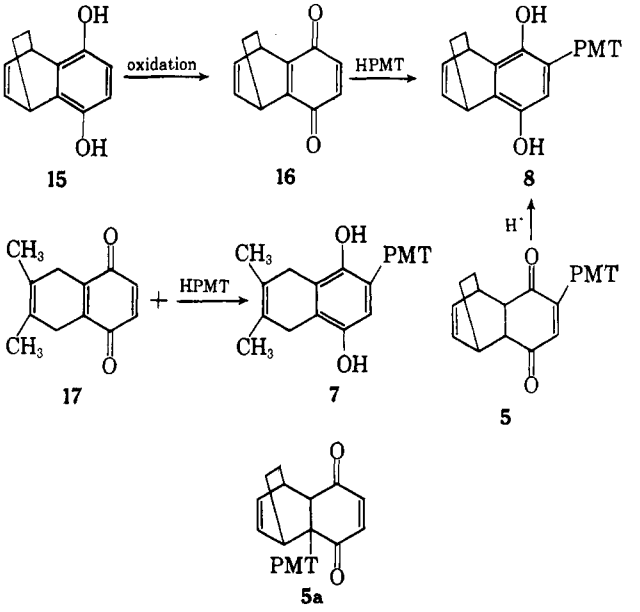
DIENE ADDUCTS. 4a,5,8,8a-TETRAHYDRO-1,4-NAPHTHOQUINONES



R	X	Compd. no.	Yield, %	M.p., °C. (crystn. solvent)	Analysis, %	Calcd.	Found
PMT		4	64–80[a]	127–129 dec. (ethanol)	C H N	62.3 5.0 15.3	62.5 4.8 15.7
PMT		5	78[a]	136–137 dec. (ethanol)	C H N S	62.6 4.4 15.4 8.8	62.7 4.0 15.0 9.1
PMT		6	81[b]	133–134 dec. (ethanol)	C H N	61.7 4.0 16.0	62.2 4.0 16.3
CH_3		18	64[a]	83–84 (ethanol)	C H	77.3 6.9	77.6 7.2
C_6H_5		19	84[a]	92–93 (ligroin)	C H	81.8 6.1	81.5 6.3
C_6H_5		30	55–70[b]	70–71 (ethanol–water)	C H	81.7 5.6	82.1 5.8

[a] Refluxed for 16 hr. in benzene. [b] For 24 hr. at room temperature; refluxed for 8 hr. in benzene.





The infrared spectra of the hydroquinone derivatives (**7**–**9**) showed no absorption in the carbonyl region but did show strong hydroxyl absorption.

An independent synthesis of hydroquinone **8** was afforded by the addition of HPMT to quinone **16**[11,13] prepared by ferric chloride oxidation of hydroquinone **15**.[11] Adduct **5** thus would have the structure shown. Structure **5a** appears improbable, since the acid rearrangement to hydroquinone **8** would require a mercaptan migration.

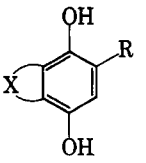
Dimethylbutadiene adducts can be employed in a similar manner. The structure of hydroquinone **7** obtained by the acid rearrangement of the 2,3-dimethylbutadiene-*p*-benzoquinone adduct (**4**) also was confirmed by this method. The mercaptan (HPMT, **1**) was added to 6,7-dimethyl-5,8-dihydro-1,4-naphthoquinone (**17**) to produce hydroquinone **7**.

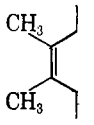
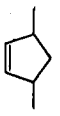
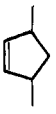
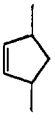
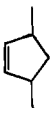
Two additional cyclohexadiene adducts were prepared by this procedure, rearranged with acid, oxidized

(13) M. Lora-Tamayo and J. L. Leon, *J. Chem. Soc.*, 1499 (1948).

TABLE IV

5,8-DIHYDRO-1,4-NAPHTHOHYDROQUINONES



R	X	Compd. no.	Yield, %	M.p., °C. (crystn. solvent)	Analysis, % Calcd.	Found
PMT		7	70–90[a]	185–186 dec. (ethanol)	C 62.3 H 5.0 N 15.3	62.5 4.9 15.7
PMT		8	90[a]	204–205 dec. (50% acetic acid)	C 62.6 H 4.4 N 15.4 S 8.8	62.6 4.5 15.4 8.9
PMT		9	29[b]	182–183 dec. (isopropanol)	C 61.7 H 4.0 N 16.0 S 9.1	61.4 4.1 15.9 9.0
CH_3		20	85[a]	180–182 (50% acetic acid)	C 77.3 H 6.9	76.9 7.2
C_6H_5		21	68[a]	172–172.5 (benzene–ligroin)	C 81.8 H 6.1	81.6 6.2
CH_3[c]		31	53[d]	168–169 (50% acetic acid)	C 76.6 H 6.4	76.1 6.1
C_6H_5		32	78[d]	164–165 (50% acetic acid)	C 81.7 H 5.6	81.6 5.8
H[c]		28[e]	46[f] 47.5[g]	143–144 (ethyl acetate–ligroin) 143–145 (ethyl acetate–ligroin)		

[a] Ref. 10. [b] For 4 days at room temperature in benzene with catalytic amount of $(C_2H_5)_3N$. [c] See ref. 14. [d] For 12 days at room temperature in benzene with 1 mole of $(C_2H_5)_3N$. [e] See ref. 13. [f] Condition *b* for 10 days. [g] For 14 days at room temperature in ethanol with catalytic amount of $(C_2H_5)_3N$.

to the quinones, and the quinones were allowed to react with the mercaptan to produce the desired hydroquinone derivatives.[7] Toluquinone and phenylquinone reacted as expected in this sequence (see Tables II–IV).

As mentioned previously, the cyclopentadiene adducts to quinones do not rearrange readily with acid to the hydroquinones. The preparation of 5,8-dihydro-5,8-methano-1,4-naphthoquinone (**27**) by a ferric chloride oxidation in an acetic acid–mineral acid solution of adduct **26** has been reported,[11] but the yield is very low. The same quinone (**27**) was obtained by Meinwald[14] in high yield by oxidation of hydroquinone **28**, which, in turn, was obtained by a pyridine rearrangement in the presence of acetic anhydride, producing the diacetate, followed by a lithium aluminum hydride cleavage. (See scheme, p. 592, col. 1.)

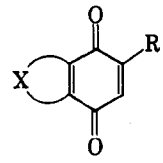
We have now found that a treatment of these cyclopentadiene adducts with triethylamine in benzene (air preferably excluded) produces the hydroquinone in reasonable yields, as listed in Table IV. The adducts of *p*-benzoquinone, toluquinone,[15] 2-phenyl-1,4-benzoquinone, and 1′-phenyl-5′-tetrazolylthio-1,4-benzoquinone (**3**) were rearranged by this method. Hydroquinones **28** and **32** from adducts **26** and **30** were oxidized to the dihydronaphthoquinones (**27**[13] and **33**) and were allowed to react with the mercaptan (**1**)

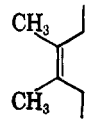
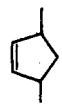
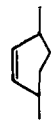
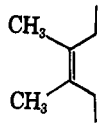
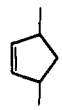
(14) J. Meinwald and G. A. Wiley, *J. Am. Chem. Soc.*, **80**, 3667 (1958).

(15) K. Alder, F. H. Flock, and H. Beumling, *Ber.*, **93**, 1896 (1960).

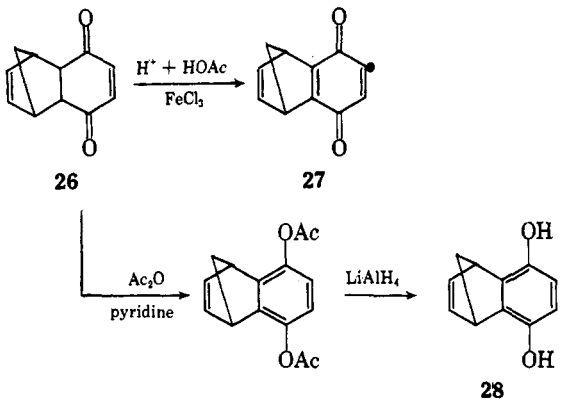
TABLE V

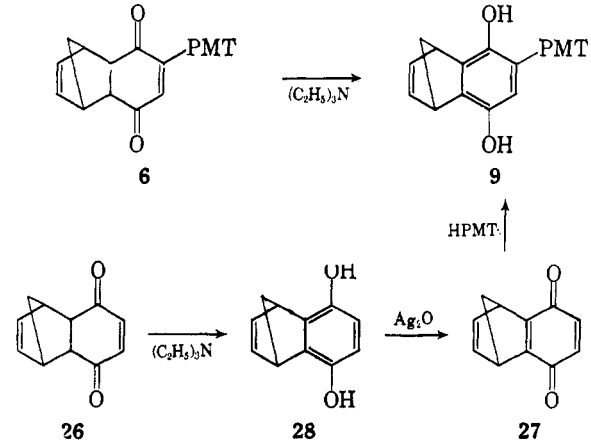
5,8-DIHYDRO-1,4-NAPHTHOQUINONES



R	X	Compd. no.	Yield, %	M.p., °C. (crystn. solvent)	Analysis, %	Calcd.	Found
PMT		10	50[a]	166–167 dec. (ethanol–acetone)	C H N S	62.7 4.4 15.4 8.8	62.7 4.1 15.3 9.1
PMT		11	60[a]	148–149 dec. (ethanol–acetone)	C H N S	63.0 3.9 15.5 8.8	62.9 4.2 15.6 8.6
PMT		12	27[b]	126–128 dec. (cyclohexane–benzene)	C H N S	62.1 3.5 16.1 9.2	61.8 3.8 15.7 9.2
CH_3		22	75[a]	82–83 (50% ethanol)	C H	78.0 6.0	77.5 6.0
C_6H_5		23	Quant.[b]	111.5–113 (ligroin, 90–110)	C H	82.4 5.4	82.4 5.7
H[c]		17	70[a]	88–90, unstable, rapidly darkens	C H	76.6 6.6	76.6 6.7
C_6H_5		33	Quant.[d]	116–118 (ethanol–water)	C H	82.2 4.9	82.2 4.8

[a] Ferric chloride in boiling ethanol. [b] Silver oxide in benzene. [c] See ref. 12. [d] Silver oxide in acetone.





to give the quinone–mercaptan adducts, *e.g.*, hydroquinones (**9** and **34**).

Quinone–mercaptan adduct **9**, obtained by reaction of the mercaptan (**1**) with quinone **27**, was identical with that obtained by the triethylamine rearrangement of the cyclopentadiene-1′-phenyl-5′-tetrazolylthioquinone adduct (**6**).

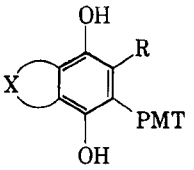
From these results we conclude that the normal Diels–Alder adducts of various quinones can be rearranged and oxidized to their substituted quinones, which, in turn, undergo 1,4-addition reactions with mercaptans.

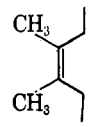
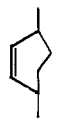
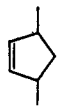
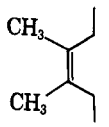
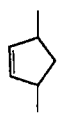
Experimental

Unless otherwise specified, all chemicals are Eastman Kodak Company materials.

TABLE VI

MERCAPTAN-SUBSTITUTED QUINONE ADDUCTS



R	X	Compd. no.	Yield, %	M.p., °C. (crystn. solvent)	Analysis, %	Calcd.	Found
PMT		13	67[a]	191–192 dec. (dioxane–acetone)	C	57.6	57.8
					H	4.1	4.3
					N	20.7	20.6
					S	11.8	11.4
PMT		14	75[a]	191–192 dec. (chloroform–cyclohexane)	C	57.8	58.1
					H	3.7	3.9
					N	20.7	21.0
					S	11.8	11.6
CH_3		24	90[b]	185–186 dec. (50% acetic acid)	C	63.5	63.1
					H	4.8	4.8
					N	14.8	14.5
					S	8.5	8.5
C_6H_5		25	69[c]	199.5–200.5 dec. (isopropyl alcohol)	C	68.2	68.2
					H	4.6	4.9
					N	12.7	12.8
					S	7.3	7.3
H[d]		9	86[a]	184 dec.[e]			
H		7	55[c]	185–186 dec.[e]			
C_6H_5		34	88[f]	125–136 (acetic acid)	C	67.3	67.2
					H	4.7	4.5
					N	13.1	12.9
					S	7.5	7.6

[a] Refluxed for 24 hr. in chloroform. [b] Refluxed for 18 hr. in ethanol. [c] Refluxed for 3 hr. in ethanol. [d] See ref. 13. [e] See Table IV. [f] For 18 hr. at room temperature in ethanol–chloroform.

Substituted Hydroquinones and Catechols.—The addition of HPMT (1) to the various 1,4- and 1,2-benzoquinones was usually carried out by adding the quinone to the mercaptan in a suitable solvent. The details are listed in Tables I and II. Illustrative examples are given in the next three sections.

(1′-Phenyl-5′-tetrazolylthio)hydroquinone (2).—A suspension of 143 g. of HPMT in 500 ml. of methanol was stirred and cooled in an ice–water bath. To this was added 86.5 g. of *p*-benzoquinone in approximately 20-g. portions. The temperature was maintained below 20°, and the mixture was allowed to cool to 10° before the addition of the next portion of *p*-benzoquinone. After addition was complete, the mixture was stirred at room temperature for 2.5 hr. The solid materials were collected by suction filtration, washed with methanol, and air-dried to yield 218 g. (94%) of white solid, m.p. 211–212° dec.

A portion of the product was crystallized from acetone to yield white prisms, m.p. 216–217° dec.

Anal. Calcd. for $C_{13}H_{10}O_2N_4S$: C, 54.5; H, 3.5; N, 19.6; S, 11.2. Found: C, 54.9; H, 3.8; N, 20.0; S, 11.2.

2-(1′-Phenyl-5′-tetrazolylthio)-6,7-dimethyl-5,8-dihydro-1,4-naphthohydroquinone (7). Method A.—A solution of 1.88 g. of 6,7-dimethyl-5,8-dihydro-1,4-naphthoquinone (17) and 1.78 g. of HPMT in 40 ml. of alcohol was refluxed for 2 hr. and then chilled. The precipitate was collected and dried. The yield was 2.0 g., m.p. 181–183° dec.; after recrystallization from alcohol, m.p. 183–185° dec. The mixture melting point with the material prepared by method B was not depressed; the infrared spectra were identical.

2-(1′-Phenyl-5′-tetrazolylthio)-5,8-dihydro-5,8-ethano-1,4-naphthohydroquinone (8). Method A.—A solution of 1.86 g. of 5,8-dihydro-5,8-ethano-1,4-naphthoquinone (16)[11] and 1.78 g. of HPMT in 10 ml. of alcohol was refluxed for 2 hr., during which time the color disappeared. The clear solution was evaporated to dryness, and the residue was taken up in 15 ml. of hot 50% acetic acid and chilled. The crystals were filtered and dried. The yield was 2.0 g., m.p. 189–193° dec.; after several recrystallizations, m.p. 199–201° dec. The mixture melting point with material prepared by method B was not depressed; the infrared spectra of the two were identical.

Substituted Quinones.—The substituted quinones were prepared by oxidation methods from the corresponding hydroquinones; the details are listed in Table V. An illustrative example is given in the next section.

(1′-Phenyl-5′-tetrazolylthio)-1,4-benzoquinone (3).—(1′-Phenyl-5′-tetrazolylthio)hydroquinone (143 g.) was added to a solution, 30.4 g. of sodium chlorate in 2.3 l. of acetic acid and 685 ml. of 2% sulfuric acid. The suspension was stirred for 5 hr. at 35–40°, during which time the suspended material dissolved and partially reprecipitated as a bright yellow solid. The suspension was poured into ice–water (7.5 l.), with stirring, and the solid material

was collected on a filter, washed twice with 50-ml. portions of alcohol, and dried. The yield was 123 g., m.p. 156–158° dec.; recrystallized from alcohol, m.p. 157–158° dec.

Anal. Calcd. for $C_{13}H_8O_2N_4S$: C, 54.9; H, 2.8; N, 19.7. Found: C, 55.1; H, 3.1; N, 19.8.

Diene–Quinone Adducts.—The diene–quinone adducts (Table III) were usually prepared in benzene. A preparative example is given in the next section.

2-(1′-Phenyl-5′-tetrazolylthio)-4a,5,8,8a-tetrahydro-5,8-ethano-1,4-naphthoquinone (5).—A solution of 2.6 g. of cyclohexadiene and 8.5 g. of (1′-phenyl-5′-tetrazolylthio)-1,4-benzoquinone (**3**) in 100 ml. of benzene was refluxed for 16 hr. and evaporated to a heavy oil. The oil was taken up in 100 ml. of hot alcohol, filtered, and chilled. The crystals were collected and dried. The yield was 8.5 g., m.p. 132–134°; recrystallized from alcohol, m.p. 136–137°.

Anal. Calcd. for $C_{19}H_{16}O_2N_4S$: C, 62.6; H, 4.4; N, 15.4; S, 8.8. Found: C, 62.7; H, 4.3; N, 15.0; S, 8.9.

5,8-Dihydronaphthohydroquinones by Rearrangement of Adducts.—The acid-catalyzed rearrangement of the dimethylbutadiene and 1,3-cyclohexadiene–quinone adducts was carried out by the procedure of Diels and Alder[11]; the experimental conditions are listed in Table IV. Illustrative examples are given in the next two sections.

2-(1′-Phenyl-5′-tetrazolylthio)-6,7-dimethyl-5,8-dihydro-1,4-naphthohydroquinone (7). Method B.—A suspension of 2.0 g. of **4** in 10 ml. of acetic acid was treated with 3 drops of 48% hydrobromic acid and warmed gently on a steam bath. Within 2 min. the material dissolved, white crystals appeared, and the mixture solidified. A 10-ml. portion of 50% acetic acid was added, the mixture was stirred and chilled, and the crystals collected and washed with water. The yield was 1.4 g., m.p. 181–183° dec.; after two recrystallizations from alcohol, m.p. 185–186° dec.

Anal. Calcd. for $C_{10}H_{18}O_2N_4S$: C, 62.3; H, 5.0; N, 15.3; S, 8.7. Found: C, 62.7; H, 5.0; N, 15.6; S, 9.0.

2-(1′-Phenyl-5′-tetrazolylthio)-5,8-dihydro-5,8-ethano-1,4-naphthohydroquinone (8). Method B.—A suspension of **5** (4.0 g.) in 20 ml. of acetic acid was treated with 8 drops of 48% hydrobromic acid and warmed on the steam bath for 10 min. The resulting solution was then diluted with 15 ml. of hot water and the mixture was chilled. The white crystals were collected, washed with water, and dried. The yield was 3.7 g., m.p. 192–194° dec.; after repeated recrystallization from 50% acetic acid, m.p. 204–205° dec.

Anal. Calcd. for $C_{19}H_{16}O_2N_4S$: C, 62.6; H, 4.4; N, 15.4; S, 8.8. Found: C, 62.6; H, 4.5; N, 15.4; S, 8.9.

Rearrangement of the Cyclopentadiene–Quinone Adducts.—The triethylamine rearrangement of the cyclopentadiene–quinone adducts is illustrated by the example given in the next section; experimental details for the other similar materials are listed in Table IV.

2-Phenyl-5,8-dihydro-5,8-methano-1,4-naphthohydroquinone (32).—A solution of 10 g. of adduct **30** and 4 g. of triethylamine in 50 ml. of benzene was allowed to stand for 12 days at room temperature under nitrogen. If the hydroquinone had not crystallized at the end of this time, the solution was diluted with 50 ml. of ether and washed twice with 50 ml. of 10% sodium hydroxide solution, and the combined washings were acidified to precipitate hydroquinone **32**. The yield, after two recrystallizations from 50% acetic acid, was 7.8 g., m.p. 164–165°.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.7; H, 5.6. Found: C, 81.6; H, 5.8.

The infrared spectrum showed strong hydroxyl absorption and no absorption in the carbonyl region.

5,8-Dihydro-1,4-naphthoquinone Derivatives.—The substituted 5,8-dihydro-1,4-naphthoquinones were prepared by ferric chloride or silver oxide oxidation of the corresponding 5,8-dihydro-1,4-naphthohydroquinones; the details are listed in Table V. Preparative examples are given in the next two sections.

6,7-Dimethyl-5,8-dihydro-1,4-naphthoquinone (17).—A suspension of 3.0 g. of 6,7-dimethyl-5,8-dihydro-1,4-naphthohydroquinone[10] in 40 ml. of hot alcohol was mixed with 9.0 g. of ferric chloride in 50 ml. of hot alcohol, and the resulting mixture was boiled for 5 min. and poured into 400 ml. of ice–water. The yellow crystals were filtered and quickly dried under vacuum. The yield was 2.2 g., m.p. 88–90°.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.6; H, 6.6. Found: C, 76.6; H, 6.7.

The quinone was very unstable and darkened rapidly on exposure to air.

2-Phenyl-5,8-dihydro-5,8-methano-1,4-naphthoquinone (33).—Fifty milliliters of acetone was added to 7.55 g. of 2-phenyl-5,8-dihydro-5,8-methano-1,4-naphthohydroquinone (**32**) to give a solution to which 5.0 g. of anhydrous sodium sulfate and then 15 g. of silver oxide was added, with stirring. After 8 min., the slurry was filtered using Filter-Cel, and the acetone was removed under reduced pressure. The resulting yellow oil crystallized to give a quantitative yield of quinone **33**, m.p. 107–109°; recrystallization from alcohol–water gave yellow needles, m.p. 116–118°.

Anal. Calcd. for $C_{17}H_{12}O_2$: C, 82.2; H, 4.9. Found: C, 82.5; H, 5.2.

Substituted Mercaptan–Quinone Adducts.—The substituted mercaptan–quinone adducts were usually prepared by mixing equimolar amounts of the mercaptan (**1**) and the 5,8-dihydro-1,4-naphthoquinone in a suitable solvent. The various products are listed in Table VI.

The Chemistry of Thioether-Substituted Hydroquinones and Quinones. II. Substituent Effects in the 1,4-Addition of a Heterocyclic Mercaptan to Monosubstituted Quinones

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The 1,4-addition of 1-phenyl-5-mercaptotetrazole to monosubstituted 1,4-benzoquinones gave a 2,3, 2,5, or 2,6 disubstituted hydroquinone or a mixture of isomeric products. Strong electron-donating groups direct the mercaptan to the 5-position while weak electron-donors direct the mercaptan to both the 5- and the 6-position. Strong electron-withdrawing groups direct the mercaptan to the 3-position. The only weak electron-withdrawing group investigated gave all three isomers. The steric effect of the substituent was demonstrated for the 3-position of the quinone ring.

Discussion

The preceding paper in this series[1] was concerned with unsubstituted, disubstituted, and trisubstituted 1,4-benzoquinones and their reactions with a heterocyclic mercaptan. These quinones did not involve isomeric products. However, the 1,4-addition of a mercaptan to monosubstituted 1,4-benzoquinones could give one of three possible isomers, the 2,3, the 2,6, or the 2,5 compound, or a mixture of them. The mechanism of this reaction is unknown but is presumed to involve a nucleophilic attack on the quinone ring. A free-radical mechanism does not appear likely in view of the highly acidic nature of this mercaptan and the free-radical-

(1) R. F. Porter, W. W. Rees, E. Frauenglass, H. S. Wilgus, III, G. H. Nawn, P. P. Chiesa, and J. W. Gates, Jr., *J. Org. Chem.*, **29**, 588 (1964).