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).

inhibiting character of the hydroquinone products. Since we can ignore variation in mercaptan properties, only two factors should be involved, the steric nature of the quinone substituent and its electronic character. The electronic effect is straightforward for a nucleophilic reaction. Electron-donating groups should give predominantly the 2,5 isomer and secondarily the 2,6 isomer. Electron-withdrawing groups should favor formation of the 2,3 isomer, with the 2,6 isomer a second choice.

The steric effect is readily visualized with the aid of molecular models. Steric factors should involve only the 3-position and not the 5- and 6-positions across the ring. Therefore, the effect of electron-donating groups should be free of steric influences while the effect of electron-withdrawing groups should exhibit some sensitivity to steric factors.

Investigations of the directive influence of substituents on quinones when subjected to addition reactions are not new. Erdtman[2] reported studies on electron-donating groups in the Thiele acetylation reaction. He studied a variety of combinations of $-CH_3$ and $-OCH_3$ and from these results he showed that $-OCH_3$ directs the entering group strongly *para* and, if that position is blocked, that no reaction will occur. If $-CH_3$ and $-OCH_3$ are competing, the $-OCH_3$ dominates in directing the entering group in the formation of products.

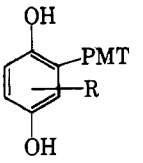
The early literature concerning the addition of hydrogen halides to quinones is confusing and contradictory. In 1950 Cason and co-workers[3] did much to clarify this confusion by showing that attempts to separate and identify the components of the mixtures of isomers had been and remained unsuccessful.

Other addition reactions to quinones are those with amines[4] and mercaptans.[5] Posner's[5b] extensive work on mercaptan addition indicated that disubstituted hydroquinones were the normal products to which he assigned the 2,5 structure on a dialectic basis. He was able to isolate a second isomer from one reaction to which he assigned the 2,6 structure on the same basis. Later workers[5c,d,g] studying analogous disubstituted hydroquinones apparently have assumed the validity of the 2,5 structure, and no further reports of more than one product have been found.

The mercaptan used in this study was the same as that used in the previous paper,[1] 1-phenyl-5-mercaptotetrazole, hereafter abbreviated as HPMT. The results of our study are compiled in Table I. The general method of isolation and identification of these products involved fractional crystallization, followed by n.m.r. studies. The low thermal stability of these adducts precluded the use of v.p.c. Some of these hydroquinones could not be identified by n.m.r., since the spin–spin coupling of the ring hydrogens could not be resolved. Oxidation to the quinones in most cases did give compounds having measurable coupling constants. The spin–spin couplings observed for the quinones as well as the hydroquinones were the same as those given for benzene by Jackman[6]: *para* 1, *meta* 2–3, and *ortho* 7–10 c.p.s. Some brief comments on the preparation and identification of the products obtained are made.

TABLE I

YIELDS AND N.M.R. COUPLING CONSTANTS OF ISOMERIC MONOSUBSTITUTED 1,4-BENZOQUINONE–HPMT ADDUCTS

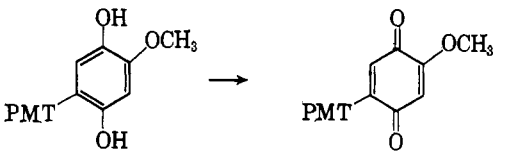


	Isomer					
	Yields, %			Coupling constants, c.p.s.		
R	2,3	2,5	2,6	2,3	2,5	2,6
$-OCH_3$		88			$<1^{c,d}$	
$-4'-C_6H_4OCH_3$		80			<1	
$-CH_3$		25	13			2.5^d
$-C_{15}H_{31}$		48	12		$<1^d$	2.2^d
$-4'-C_6H_4CH_3$		10	30		$<1^d$	2.5^d
$-C_6H_5$		10^a	46^a		$<1^{c,d}$	$2.5,^d$ 2.9^e
–PMT	28^a	20^a	26^a			
$-4'-C_6H_4NO_2$			82			$2.4,^d$ 3.0^e
$-4'-C_6H_4COCH_3$	?	?	36			2.7^e
$-COCH_3$	74		8^b	9.3^e		
$-COOCH_3$	91			9.2^e		

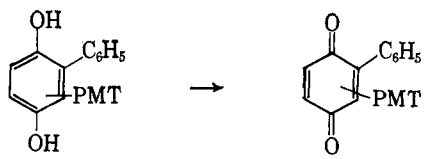
[a] Highest yield obtained from multiple runs. [b] Not isolated but identified by nuclear magnetic resonance (n.m.r.). [c] N.m.r. coupling constants on the hydroquinone. [d] N.m.r. coupling constants on the oxidized hydroquinone. [e] N.m.r. coupling constants on the dimethyl derivatives.

When HPMT was added to methoxyquinone, a high yield of only one product was obtained. This product, the disubstituted hydroquinone (**1**), was oxidized to the corresponding quinone (**2**). N.m.r. studies of hydroquinone **1** and quinone **2** showed these to be the 2,5 isomer.

When HPMT was added to phenylquinone, two isomeric hydroquinones, **3** and **4**, were isolated. Both isomers were oxidized to their corresponding quinones, **5** and **6**. Quinone **5** showed the *para* spin–spin coupling of the dissimilar ring hydrogens by n.m.r. and hence has the 2,5 configuration. Quinone **6** was identified by n.m.r. as the 2,6 isomer.



1 **2**



3 and **4** **5** and **6**

The addition of HPMT to 4′-methylphenylquinone also gave two isomeric hydroquinones, **7** and **8**. Although the position of substitution of **8** could not be

(2) H. G. H. Erdtman, *Proc. Roy. Soc.* (London), **A143**, 177 (1933–1934); *Anales soc. españ. fis. quim.*, **32**, 614 (1934).

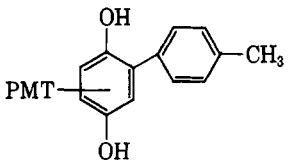
(3) J. Cason, R. E. Harman, S. Goodwin, and C. F. Allen, *J. Org. Chem.*, **15**, 860 (1950).

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

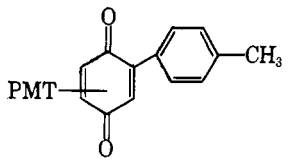
(5) (a) J. Troeger and A. Eggert, *J. prakt. Chem.*, [2]**53**, 478 (1896); (b) T. Posner, *Ann.*, **336**, 85 (1904); (c) J. M. Snell and A. Weissberger, *J. Am. Chem. Soc.*, **61**, 450 (1939); (d) O. Dimroth, L. Kraft, and K. Aichinger, *Ann.*, **545**, 124 (1940); (e) R. Kuhn and H. Beinert, *Ber.*, **77**, 606 (1944); (f) M. Schubert, *J. Am. Chem. Soc.*, **69**, 712 (1947); (g) H. Burton and S. B. David, *J. Chem. Soc.*, 2193 (1952).

(6) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 85.

established from the n.m.r. spectrum, the magnitude of the coupling constant of a slightly impure sample of **7** suggested 2,5 substitution. Pure hydroquinone **7** was obtained by reduction of quinone **9**. Quinones **9** and **10** were prepared and identified by n.m.r.



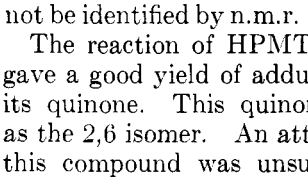
7 and **8**



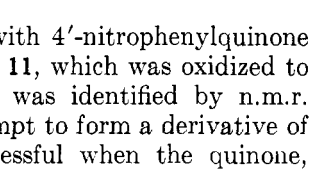
9 and **10**

When the substituent R (Table I) was $-4'-C_6H_4-COCH_3$, a product was obtained which appeared to be a single compound. However, this could not be identified by n.m.r. Conversion to a rearranged dimethyl derivative[7] analogous to **12** showed two isomers to be present. The major product was identified as the 2,6 isomer by n.m.r.; the minor product could not be identified by n.m.r.

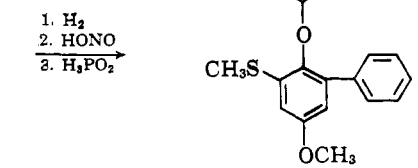
The reaction of HPMT with 4′-nitrophenylquinone gave a good yield of adduct **11**, which was oxidized to its quinone. This quinone was identified by n.m.r. as the 2,6 isomer. An attempt to form a derivative of this compound was unsuccessful when the quinone, a crystalline but unstable material, failed to undergo a Diels–Alder reaction with 1,3-cyclohexadiene. That 4′-nitrophenylquinone did not give the 2,3 isomer is probably due to the steric effect of the phenyl ring. A steric effect was also probably responsible for the lack of reactivity of 2,5-di-*t*-butyl-[1] and 2,5-diphenylquinone with HPMT. That no reaction occurred is probably due to the blocking effect of the substituents. The 2,6 structure for the 4′-nitrophenyl-PMT-hydroquinone was proved chemically by its conversion to its dimethyl derivative (**12**), followed by reduction, diazotization, and replacement of the diazo group with hydrogen to give **13**. This same product was synthesized from the previously prepared 2-phenyl-6-(1′-phenyl-5′-tetrazolylthio)hydroquinone (**6**) by treatment with methyl iodide.



11



12

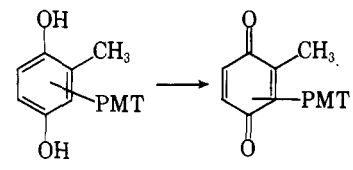


13

(7) The proof of structure for this type of unexpected product will be the topic of a forthcoming publication. The apparent migration of the 1-phenyl-5-tetrazoyl group from sulfur to oxygen does not change the location of the phenyl protons which are being investigated by n.m.r.

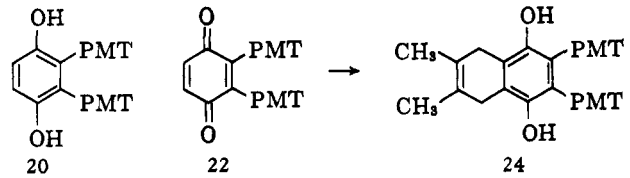
In two cases, R = $-COOCH_3$ and $-COCH_3$, the hydroquinone products gave no coupling constants and attempts to oxidize them to the quinones with Ag_2O, $FeCl_3$, and $NaClO_3$ were unsuccessful. The hydroquinones were identified by n.m.r. after they had been converted to their dimethyl derivatives. By n.m.r. studies, a second product, the 2,6 isomer in 8% yield, was found and identified when R was $-COCH_3$. The isomer was not isolated.

The addition of HPMT to toluquinone gave two compounds, **14** and **15**, which could not be identified by n.m.r. The compounds were oxidized to their quinones, **16** and **17**, and then condensed in a Diels–Alder reaction with 1,3-cyclohexadiene.[8] In both cases the products were oils. Acid treatment of these oils failed to give a crystalline product. The 2,6-quinone (**17**) was identified by n.m.r., and the 2,5 isomer was identified by the process of elimination when an independent synthesis of a derivative of the 2,3 isomer (**18**), its Diels-Alder adduct with cyclohexadiene, was completed.[1] Infrared spectra of the last compound did not correspond with those of the adducts obtained from the preceding isomers, thus eliminating the 2,3 isomer as an isolated reaction product.

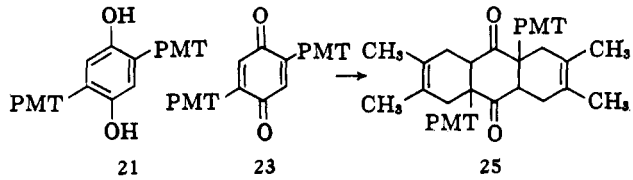


14 and **15** **16** and **17** **18**

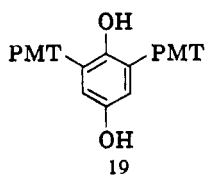
Reaction of HPMT with 2-(1′-phenyl-5′-tetrazolylthio)quinone gave a mixture from which three isomers were obtained. One of these products, **19**, could not be oxidized and was identified as the 2,6 isomer by n.m.r., which showed the presence of dissimilar hydroxyl hydrogens. The oxidation products, quinones **22** and **23** of the other two hydroquinones **20** and **21**, were condensed with 1 mole of 2,3-dimethylbutadiene to give, in one case, a monoadduct (**24**) in high yield which had rearranged to its hydroquinone; and in the other, a diadduct (**25**) in low yield. The quinone (**23**) which gave the diadduct could not be condensed to give a monoadduct, thus indicating that it was the 2,5



20 **22** **24**



21 **23** **25**



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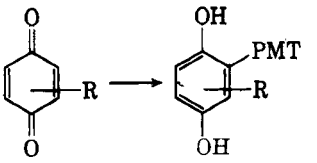
(8) O. Diels and K. Alder, *Ber.*, **62**, 2337 (1929).

TABLE II

HYDROQUINONES

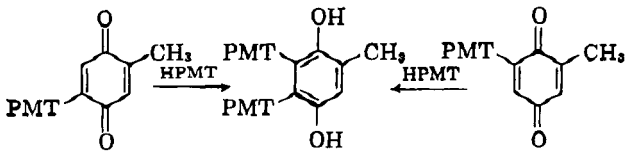


	Parent quinone	Reaction conditions, hr., °C.	Yield, %	M.p. dec., °C.	Crystn. solvent		Analysis, % Calcd.	Found
5-OCH_3	*a*	2, 0, in alcohol	80	193–194	*p*-Dioxane	C	53.2	53.5
						H	3.8	4.0
						N	17.7	17.9
						S	10.1	9.9
3-$COCH_3$	*b*	2, 0, in alcohol–chloroform	82	190–194		C	54.9	55.0
						H	3.7	3.9
						N	17.1	17.0
						S	9.7	9.7
3-$COOCH_3$	*c*	2, 0, in alcohol–chloroform	90	172–173	Methanol	C	52.3	51.9
						H	3.5	3.6
						N	16.3	16.5
						S	9.3	9.4
6-(4′-$C_6H_4NO_2$)	*d*	0.5, room temp., in methanol	82	223–226	Ethanol–water	C	56.0	55.9
						H	3.2	3.3
						N	17.1	16.6
						S	7.9	7.7
5-(4′-$C_6H_4OCH_3$)	*d*	4, room temp., in alcohol–chloroform	80	188–190		C	61.2	61.2
						H	4.1	4.1
						N	14.3	14.4
						S	8.2	8.2

[a] J. A. D. Jeffreys, *J. Chem. Soc.*, 2155 (1959). [b] M. C. Kloetzel, R. P. Dayton, and B. Y. Abadir, *J. Org. Chem.*, **20**, 38 (1955). [c] J. Cason, "Organic Reactions," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 355. [d] P. Brassard and P. L'Ecuyer, *Can. J. Chem.*, **36**, 700 (1958).

isomer. The monoadduct was shown to be the 2,3 isomer by an independent synthesis of **24**,[1] the Diels–Alder adduct with 2,3-dimethylbutadiene.

Since the methyl group of toluquinone appears to direct an entering group primarily to the 5-position and secondarily to the 6-position and the PMT group in 2-(1′-phenyl-5′-tetrazolylthio)quinone appears to direct an entering group predominantly to the 3-position, the addition of HPMT to quinones **16** and **17** should result in high yields of the same compound. Both quinones were observed to give the same compound (**26**) in high yields.



16 **26** **17**

To check the effect of the pH on these addition reactions, HPMT was added to 2-(1′-phenyl-5′-tetrazolylthio)quinone in acetic acid. The same ratio of isomers in somewhat higher yield was obtained as when alcohol was used as the reaction solvent.

The results of this study listed in Table I show that electron-donating groups favor 2,5 substitution and secondly 2,6 substitution, but not 2,3 substitution. Electron-withdrawing groups favor 2,3 substitution. The steric factor, essentially the same in five cases, 4′-methoxyphenyl-, 4′-methylphenyl-, phenyl-, 4′-nitrophenyl-, and 4′-acetophenylquinones, was important only in the case where the substituent was electron-withdrawing.

A note of caution is necessary in reading this table in that one cannot with certainty postulate a major directing influence if the basis is founded on isolated yields which result in a low, total recovery. This means that the yields of products from methyl-, 4′-acetophenyl-, and 4′-methylphenylquinones are of doubtful significance. This also applies, but to a lesser degree, for the products obtained from phenyl- and pentadecylquinones.

Although we did not repeat Posner's earlier work,[5b] our results indicate that his structure assignments were valid. This means that most of the later structure assignments based on Posner's study are also probably correct.

Experimental

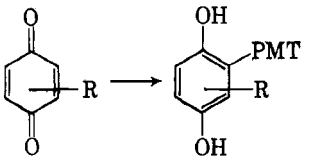
The experimental details concerned with the preparations of the hydroquinones obtained by addition of HPMT to the various quinones in which only a single product or isomer was isolated are listed in Table II. The simple preparative examples in which separations of isomers are involved are described in Table III, and the remaining examples are described in detail.

The preparation of the quinones is detailed in Table IV and details for the preparation of the dimethyl derivatives of the hydroquinones are listed in Table V. Unless specified otherwise, all reagents were Eastman Kodak Company chemicals. Melting points are corrected.

2-(4′-Methylphenyl)-5-(1′-phenyl-5′-tetrazolylthio)hydroquinone (7) from 2-(4′-Methylphenyl)-5-(1′-phenyl-5′-tetrazolylthio)-quinone (9).—To a solution of 0.25 g. of quinone 9 in 10 ml. of acetone was added 0.20 g. of stannous chloride in 1 ml. of concentrated hydrochloric acid to give an immediate loss of color. After the solution had been mixed for 1 min., it was poured into 15 ml. of water. The acetone was removed on a rotary evapora-

TABLE III

MIXTURES OF ISOMERIC HYDROQUINONES



R	Reaction conditions	Method of separation	Isomer	Crystn. solvent	M.p. dec., °C.	Analysis, %	Calcd.	Found
C_6H_5	6 hr. reflux in methanol	1. Carbon treatment + concentration	2,5	Alcohol	173–174	C	63.0	62.8
						H	3.9	4.2
						N	15.5	15.2
						S	8.8	8.5
		2. Remove HPMT with $NaHCO_3$ extn.	2,6	Alcohol	191–192			63.0
								4.0
								15.1
								8.7
4′-$C_6H_4CH_3$	6 hr. reflux in methanol	1. Carbon treatment	2,6	Alcohol	195–196	C	63.7	63.6
		2. Remove HPMT with $NaHCO_3$ extn.				H	4.3	4.1
						N	14.9	15.1
						S	8.5	8.1
		3. Concentrate mother liquors	2,5	Chloroform–petr. ether (b.p. 66–75°)	181–182			63.4
								4.1
								15.0
								8.4
CH_3	3 days, 10°, in alcohol	1. Recrystn. from chloroform	2,5	Acetone–chloroform	203–204	C	56.0	56.0
		2. Successive recrystn.				H	4.0	4.7
						N	18.7	18.7
						S	10.7	10.7
		3. Successive recrystn. of first filtrate of 2	2,6	Methanol	179–180			55.8
								4.1
								19.1
								10.7
$C_{15}H_{31}$	5.5 hr. reflux in methanol	1. Filtration	2,5	Alcohol	159–161	C	67.7	67.7
						H	8.1	8.1
						N	11.2	
						S	6.5	
		2. Concentrate filtrates + discard the solid	2,6	Alcohol	85–90			67.7
								8.3
								11.2
								6.0
PMT	5 hr. reflux in methanol	1. Filter hot	2,6		184–185	C	52.0	51.9
		2. Concentrate filtrate				H	3.1	2.9
						N	24.2	24.2
		3. Hot acetone extn. of solid from 1	2,3		212–213			51.5
								3.3
								24.8
		4. Dilute filtrate with alcohol and conc.	2,5		205–206			51.8
								3.3
								24.8

tor, and the oily residue was taken up in aqueous ethanol. Cooling in ice gave 0.21 g. of a cream-colored solid, m.p. 177–180° dec. Recrystallization from ethanol–water gave product with m.p. 184–186° dec.

Anal. Calcd. for $C_{20}H_{16}N_4O_2S$: C, 63.8; H, 4.3; N, 14.9; S, 8.5. Found: C, 63.8; H, 4.6; N, 14.6; S, 8.4.

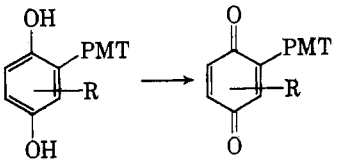
3-(4′-Acetylphenyl)-5-methylthio-4-(1′-phenyl-5′-tetrazolyloxy)-anisole and 3-(4′-Acetylphenyl)-X-methylthio-4-(1′-phenyl-5′-tetrazolyloxy)anisole.—A slurry consisting of 5.0 g. of 4′-acetylphenylquinone and 4.0 g. of HPMT in 50 ml. of cold glacial acetic acid was stirred at room temperature. The suspended solids slowly dissolved over a 10-min. period to give a clear, deep red solution. Then a dark yellow solid precipitated. This mixture was stirred for 30 min., then filtered to give 5.15 g. of a light purple powder, m.p. 186–189° dec. Extensive recrystallization from ethanol using Norit gave what appeared to be a single product as off-white nodules, m.p. 201–202° dec.

Anal. Calcd. for $C_{21}H_{16}O_3N_4S$: C, 62.4; H, 4.0; N, 13.9; S, 7.9. Found: C, 62.1; H, 4.0; N, 13.7; S, 8.1.

A 6.9-g. sample of the adduct prepared as just described was suspended in 150 ml. of dry acetone. To this slurry were added 5.0 ml. of methyl iodide and 11.0 g. of potassium carbonate to give a dark brown-green mixture. This mixture was refluxed overnight, becoming light tan in color. The acetone was removed under vacuum, and the resulting solid residue was dissolved in water and ether. The layers were separated, and the aqueous layer was extracted with ether and ethyl acetate. The combined organic layers were washed with 5% hydrochloric acid, 5% sodium hydroxide, saturated sodium bicarbonate solution, and saturated salt solution, and then were filtered through anhydrous sodium sulfate. Concentration of the filtrate gave 7.24 g. of a light brown oil which solidified on trituration with alcohol. Recrystallization from ethanol, using Norit, gave two materials; the less soluble material consisted of 1.38 g. of a tan solid, m.p.

TABLE IV

QUINONES



R	M.p. dec., °C.	Yield, %	Crystn. solvent	Analysis, %	Calcd.	Found
5-OCH_3[a]	173–175.5	91		C	53.5	53.4
				H	3.2	3.2
				N	17.8	17.8
				S	10.2	10.2
5-C_6H_5[b]	177–178	60	Ethanol	C	63.4	63.4
				H	3.3	3.4
				N	15.6	16.0
				S	8.9	9.0
6-C_6H_5[b]	118–119	80	Ethanol	C	63.4	63.9
				H	3.3	3.0
				N	15.6	15.3
				S	8.9	8.8
5-(4′-$C_6H_4CH_3$)[b]	148–149	70	Ethanol	C	64.3	63.8
				H	3.7	3.7
				N	15.0	15.2
				S	8.6	8.2
6-(4′-$C_6H_4CH_3$)[b]	160–161	70	Ethanol	C	64.3	64.4
				H	3.7	4.0
				N	15.0	15.2
				S	8.6	8.6
6-(4′-$C_6H_4NO_2$)[b]	146–147.5	60 (by chromatography)		C	56.3	56.4
				H	2.7	2.9
				S	7.9	7.5
6-$C_{15}H_{31}$[c]	80–82	75	Ethanol	C	68.0	68.6
				H	7.7	7.8
				N	11.3	11.3
5-$C_{15}H_{31}$[c]	92–93.5	50	Ethanol	C	68.0	68.0
				H	7.7	8.1
5-CH_3[c]	126–127	79	Ethanol	C	56.4	56.6
				H	3.4	3.6
				N	18.8	18.7
6-CH_3[c]	117–118	55	Ethanol	C	56.4	56.3
				H	3.4	3.6
				S	10.7	10.8

[a] Oxidized by sodium chlorate in glacial acetic acid and dilute sulfuric acid. [b] Oxidized by ferric chloride in ethanol. [c] Oxidized by sodium chlorate–vanadium pentoxide in glacial acetic acid.

145–155°. Extensive recrystallization from ethanol afforded 0.58 g. of a white powder, m.p. 161–163° dec.

Anal. Calcd. for $C_{23}H_{20}O_3N_4S$: C, 63.9; H, 4.7; N, 12.9; S, 7.4; mol. wt., 432.5. Found: C, 64.1; H, 5.0; N, 13.5; S, 7.5; mol. wt., 428.

This isomer could not be identified by n.m.r. The more soluble isomer obtained in the recrystallization amounted to 4.69 g. of tan crystals, m.p. 129–133°. Extensive recrystallization of this more soluble material from ethanol gave 2.62 g. of pale yellow needles, m.p. 132–135°. N.m.r. identified this material as 3-(4′-acetylphenyl)-5-methylthio-4-(1′-phenyl-5′-tetrazolyloxy)-anisole.

Anal. Found for $C_{23}H_{20}O_3N_4S$: C, 64.1; H, 4.8; N, 13.3; S, 7.3; mol. wt., 425.

5-Methylthio-3-phenyl-4-(1′-phenyl-5′-tetrazolyloxy)anisole (13) from 5-Methylthio-3-(4′-nitrophenyl)-4-(1′-phenyl-5′-tetrazolyloxy)anisole (12).—A 3.90-g. sample of dimethyl derivative **12** in ethyl acetate solution was catalytically reduced in the presence of Raney nickel at 33.5-lb. hydrogen pressure. Reduction was complete within 15 min. After an additional 0.5 hr., the catalyst was removed by filtration with the aid of Filter-Cel. Removal of the solvent gave 3.50 g. of the amine as a pale yellow glass.

The general procedure of diazotization and reduction employed was that of Kornblum.[9] The amine was treated with a solution of 16 ml. of concentrated hydrochloric acid in 200 ml. of water to give the salt as a voluminous white precipitate. The slurry was cooled to 0–5°, then a solution of 0.6 g. of sodium nitrite in 50 ml. of water was added. The resulting yellow slurry was stirred at 0° for 1 hr., at which time diazotization appeared to be complete. The slurry was then added to 160 ml. of ice-cold 50% hypophosphorous acid. This mixture, slowly evolving a gas, was allowed to stand at 5–10° overnight to give a yellow solid precipitate. Filtration and drying afforded 3.16 g. of yellow-orange solid, m.p. 106–113°. Two recrystallizations from ethanol, using Norit, gave 0.98 g. of ivory-colored prisms, m.p. 116–119°. The mixture melting point with authentic **13**, m.p. 119.5–120°, was 116–120°. The infrared spectra of the two materials were identical.

Separation of Isomeric Quinones 22 and 23.—A suspension of 5.0 g. of materials **20** and **21**, m.p. 202–206° dec., in acetic acid, was oxidized by the same method employed for the preparation of quinones **16** and **17**. The bright yellow precipitate obtained after oxidation was extracted with either hot acetic acid or a large volume of acetone; quinone **22**, m.p. 176–177° dec., is soluble in either solvent and crystallized on cooling, yield 1.3 g.

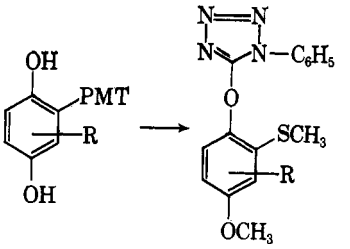
Anal. Calcd. for $C_{20}H_{12}N_8O_2S_2$: C, 52.2; H, 2.7; N, 24.4; S, 13.9. Found: C, 52.4; H, 3.0; N, 24.2; S, 13.6.

Sparingly soluble quinone **23**, m.p. 198–200° dec., may be recrystallized from a large volume of alcohol, yield 2.8 g.

(9) N. Kornblum, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 295.

TABLE V

DIMETHYL DERIVATIVES



	Reaction conditions	Yield, %	M.p. dec., °C.	Crystn. solvent		Analysis, % Calcd.	Found
3-$COCH_3$	Methyl iodide + K_2CO_3 in dry acetone, 8 hr. reflux	38	155.5–156	Alcohol	C	57.3	57.0
					H	4.5	4.6
					N	15.7	15.7
					S	9.0	9.1
6-(4′-$C_6H_4COCH_3$)	Same	90	164–165	Alcohol–acetone	C	57.9	57.1
					H	3.9	4.1
6-C_6H_5	Same	75	119–120	Alcohol–acetone	C	64.6	64.3
					H	4.6	4.6
3-$COOCH_3$	Same	30	145.5–146	Alcohol	C	54.8	54.5
					H	4.3	4.1
					N	15.1	14.8
					S	8 6	8.4

Anal. Found: C, 52.0; H, 2.6; N, 24.7; S, 13.6.

Quinone **22** may be prepared in high yield from hydroquinone **20**, m.p. 212–213° dec., obtained in the acetone separation of the impure mixture by the same oxidation method, m.p. 176–177° dec. The melting point and infrared absorption spectra were identical with those of the material obtained previously and a mixture melting point was not depressed.

One gram of quinone **23** was suspended in 15 ml. of acetic acid and stirred during the addition of 2 g. of sodium bisulfite in 5 ml. of water. The resulting suspension was allowed to stand for 2 days at room temperature, then was diluted with 10 ml. of water, and the white solid was collected. After one recrystallization from alcohol, hydroquinone **21**, 0.6 g., m.p. 203–205° dec., was obtained. The melting point and infrared spectra were identical with those of the material obtained as just described, and a mixture melting point was not depressed. Quinone **22** was similarly reduced to produce hydroquinone **20**.

2,3-Bis(1′-phenyl-5′-tetrazolylthio)-6,7-dimethyl-5,8-dihydro-1,4-naphthohydroquinone (**24**).—A solution of 1.15 g. of quinone **22** and 0.4 g. of 2,3-dimethylbutadiene in 25 ml. of benzene was refluxed for 20 hr., filtered, and evaporated to a sirup. The pale yellow sirup which contained a large amount of white crystals could not be crystallized; it was taken up in 10 ml. of hot acetic acid, and the resulting dispersion was treated with one drop of 48% hydrobromic acid and warmed for 5 min. on a steam bath. At the end of this period the mass solidified. Ten milliliters of 50% acetic acid was added, and the precipitate was filtered, washed with acetic acid, water, and alcohol, and dried; yield 1.1 g., m.p. 191–192° dec. The mixture melting point with material previously prepared[1] was not depressed and the two infrared absorption spectra were identical.

2,3,6,7-Tetramethyl-1,4,4a,5,8,8a,9a,10a-octahydro-9a,10a-di-(1′-phenyl-5′-tetrazolylthio)-9,10-anthraquinone (**25**).—A suspension of 1.15 g. of quinone **23** and 0.4 g. of 2,3-dimethylbutadiene in 50 ml. of benzene was refluxed for 24 hr., at which time the solids had dissolved. The solution was filtered and concentrated to a yellow residue. This residue was triturated with 50 ml. of hot alcohol to yield a pale yellow solid (0.5 g.), m.p. 187–188° dec.

Anal. Calcd. for $C_{32}H_{32}N_8O_2S_2$: C, 61.7; H, 5.1; N, 18.0. Found: C, 61.2; H, 5.0; N, 18.0.

Infrared absorption spectra indicated nonconjugated carbonyl groups.

3,4-Bis(1′-phenyl-5′-tetrazolylthio)tolylhydroquinone (**26**). **Method A.**—2-Methyl-6-(1-phenyl-5-tetrazolylthio)quinone (**17**) (1.0 g.), HPMT (0.63 g.), and chloroform (30 ml.) were mixed. Before solution was complete, a precipitate appeared. After standing at room temperature overnight, the white solid was filtered and washed thoroughly with chloroform to give 1.51 g. of product melting at 193–194° dec., with some decoloration at 185°. An analytical sample was prepared from ethanol.

Anal. Calcd. for $C_{21}H_{16}O_2N_8S_2$: C, 52.9; H, 3.4; N, 23.5; S, 13.4. Found: C, 53.1; H, 3.4; N, 23.5; S, 13.2.

Method B.—2-Methyl-5-(1′-phenyl-5′-tetrazolylthio)quinone (**16**) (0.60 g.), HPMT (0.38 g.), and chloroform (20 ml.) were combined. Reaction occurred more slowly than in method A. The product was treated as in method A to give 0.82 g. of fine white crystals, m.p. 187.5–189.5° dec., with darkening at 185°. Recrystallization from alcohol gave white crystals melting at 191.5–192.5° dec., with decoloration at 187°. An infrared spectrum was identical with that of the product obtained in method A.