gave on evaporation, and trituration with Et_2O, the desired product.

Compound **15** was isolated by dilution of the reaction mixture with H_2O (60 ml) and acidification with HOAc (3 ml). The mixture was extracted with $CHCl_3$, washed several times with H_2O, dried ($MgSO_4$), and evaporated to *ca.* 25 ml. Careful addition of petroleum ether caused crystallization.

Quinone **16** was isolated directly from the reaction mixture after it was chilled to 0°.

8-Amino-7-chloro-5,6-quinolinediones (17–27).—The appropriate amine (30–40 mmol) in a few millimeters of EtOH was added rapidly to a stirred solution of 3 g (13 mmol) of 7,8-dichloro-5,6-quinolinedione[9] in 400 ml of EtOH at 0°. The reaction mixture, which immediately turned deep red, was stirred for 30 min. The red quinones **17–25** were isolated directly by evaporating the solvent *in vacuo* to a volume of 25–50 ml, cooling the residual suspension to 0°, and filtering.

Compound **26** was obtained by evaporating the solvent and dissolving the resulting solid in benzene. Petroleum ether was carefully added to the point of cloudiness and the mixture chilled to 0° and filtered.

Quinone **27** was prepared using the procedure described by Zincke and Wiederhold[9] for the anilido derivative.

8-Amino-5,5,7-trichloro-6(5*H*)-quinolones (29–35).—A solution of 5,5,7,8-tetrachloro-6(5*H*)-quinolone[10] (2.5 g, 9 mmol) in 50 ml of EtOH[18] was cooled to −30° with constant stirring. The amine (27 mmol) in a few millimeters of EtOH was added rapidly. The product began to separate from the yellow-brown reaction mixture within 5 min and after 15 min the mixture was filtered to give the product as a yellow solid.

(18) A few compounds were prepared using a less polar reaction medium, see footnote *e* of Table I.

Preparation and the Results of Antitumor Screening of Some Substituted Amino-, Azido-, Halogeno- and Hydroxy-*p*-benzoquinones[1]

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Synthesis of some amino-, azido-, hydroxyl-, and halo-substituted *p*-benzoquinones are reported. The aminobenzoquinones were prepared by catalytic reduction of the corresponding azide compounds; the latter in turn were obtained by the treatment of halobenzoquinones with NaN_3. Alkylaminoquinones were prepared either by the replacement of methoxyquinones with appropriate amines or by refluxing dialkyl- or diarylbenzoquinones with amines. Some alkyl analogs of 2,5-dihydroxy-3,6-diphenyl-*p*-benzoquinone (polyporic acid) were prepared by free-radical alkylation of 2,5-dihydroxy-*p*-benzoquinone with acyl peroxide. Preliminary screening results of these compounds indicated that 2,5-diazido-3,6-dimethoxy-*p*-benzoquinone, 2,5-dichloro-3,6-diphenyl-*p*-benzoquinone, and 2,5-bis(*p*-ethylphenyl)-3,6-dihydroxy-*p*-benzoquinone possessed moderate activity against Walker carcinosarcoma 256. The last compound also possesses some activity against leukemia L-1210. Marked weight loss in the surviving animals was observed.

The antibacterial activity of many quinone derivatives has long been recognized.[2,3] This property has been attributed mainly to protein binding.[4–8] A number of benzoquinones, naphthoquinones, anthraquinones, and quinoxazines possess activity against protozoa, Gram-positive and Gram-negative bacteria, and *Mycobacterium tuberculosis*.[9] Compounds of this type are also used as antitumor agents.[9] A common *o*-aminoquinonoid unit was noted[10] among some tumor-inhibitory antibiotics such as streptonigrin, actinomycin C, mitomycins, and porfiromycin. Certain 2,5-bis(alkylamino)-3,6-dimethoxy-*p*-benzoquinones are inhibitory to sarcoma 180.[11] Polyporic acid (2,5-dihydroxy-3,6-diphenyl-*p*-benzoquinone) was reported to be active against leukemia L-1210.[12] Some quinones are potent inhibitors of dehydrogenase activity of tumor cells.[13]

It is conceivable that, in addition to the protein binding characteristics, various substituted quinones with different oxidation–reduction potentials may play an important role in the phosphorylation, H transfer, and electron transfer in biological metabolism. Selective inhibition of the tumor cells may be achieved by modification of substituents on the quinone ring system. The present communication involves the synthesis of some amino-, azido-, hydroxyl-, and halo-substituted *p*-benzoquinones and the preliminary structure–activity study in animal tumor systems.

Chemistry.—Although a series of 2,5-diaryl-3,6-dihydroxy-*p*-benzoquinones (I, R = aryl) related to polyporic acid (I, R = C_6H_5) was synthesized and evaluated by Cain,[14] the corresponding diamino analogs II have not yet been studied. In view of the importance of the aminoquinones in oncological studies,[10,11] compounds II were synthesized in this laboratory.

Since the primary amino group is susceptible to both oxidation and hydrolysis, relatively few aminoquinones were reported in the literature. By adaptation of a

(1) (a) This investigation was supported by the Cancer Chemotherapy National Service Center, National Cancer Institute, of the National Institutes of Health, Public Health Service; Contract No. PH-43-65-94; (b) presented in part before the Division of Medicinal Chemistry, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969 (MEDI 17).

(2) (a) E. A. Cooper, *Biochem. J.*, **7**, 186 (1913); (b) E. A. Cooper, *J. Soc. Chem. Ind.*, **46**, 59 (1927).

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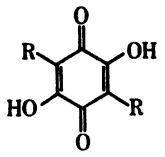
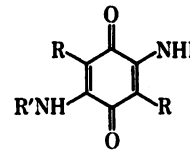
method used for the preparation of 7-amino-6-methoxy-5,8-quinolinedione,[15] the amino-*p*-benzoquinones (II, R′ = H) were successfully prepared by catalytic reduction, followed by aerial oxidation, of the corresponding azide intermediates (III), the latter in turn being obtained by the treatment of halobenzoquinones (IV) with NaN_3 in aqueous acetone. Amino-*p*-benzoquinones prepared by this method were found to be identical with those prepared by displacement of methoxy-*p*-benzoquinones (IV, X = OCH_3) with NH_3.[16] Alkylaminoquinones were prepared either by the replacement of methoxyquinones with appropriate amines[11] or by refluxing 2,5-dialkyl- or 2,5-diaryl-*p*-benzoquinones with


I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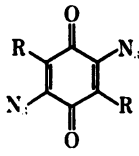
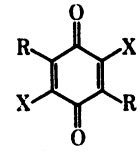
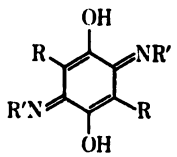
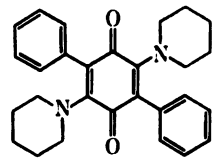

III


IV

amines.[17] Alkylamino chains of various length (C_6,C_7 to C_{14},C_{15}) were prepared so that the absorption pattern of the resulting compounds may be changed due to their different hydro-lipo distribution. For comparison of biological activity, some alkyl analogs of polyporic acid (I, R = alkyl) were prepared by free-radical alkylation of 2,5-dihydroxy-*p*-benzoquinone with acyl peroxide in AcOH.[18] The products were found to be identical with that prepared by the base-catalyzed condensation of esters of oxalic and fatty acids.[19] The corresponding aryl analogs (I, R = aryl) were obtained through diazotization of 2,5-dichloro-*p*-benzoquinone followed by hydrolysis[14a] (see Table I).

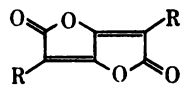
Ir spectra of these aminobenzoquinones revealed that there is a tautomerization between the amino (II) and the imino form (V) and that the imino form predominated. This is shown by the fact that for compounds such as tetrachloro-, tetramethoxy-, or 2,5-diphenyl-*p*-benzoquinone, a strong C=O absorption band[20] was observed between 1620 and 1650 cm^{-1}.

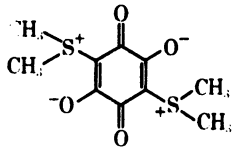

V


VI

On the other hand, with the amino derivatives such as 2,5-diamino-3,6-diphenyl- or 2,5-bis(hexylamino)-3,6-diphenyl-*p*-benzoquinone, only a trace of this characteristic band was noted together with the presence of a strong and sharp peak at 3240 cm^{-1} (OH). In the case of 2,5-diphenyl-3,6-dipiperidinyl-*p*-benzoquinone (VI) where tautomerization is not possible, thes trong 1620 cm^{-1} C=O band was again observed in the infrared spectrum. A resonance equilibrium between the amino- and imino-*p*-quinones in solution has already been noted.[11,21]

Moore and coworkers[22] reported that treatment of polyporic acid with Ac_2O in the presence of DMSO yielded 3,6-diphenyl-2*H*,5*H*-furo[3,2-*b*]furan-2,5-dione (pulvinic acid dilactone, VIIa). The latter was identical with that obtained by the oxidation of polyporic acid with $Pb(OAc)_4$.[23] Under the same reaction conditions, 2,5-dihydroxy-*p*-benzoquinone (I, R = H), however, did not yield the corresponding bis-$\Delta^{\alpha,\beta}$ butenoide VIIb, but a sulfur-containing, yellow crystalline product. The product was found to have limited solubility in organic solvents and was soluble in H_2O. Its ir spectrum showed neither hydroxyl functions nor unsaturated γ-lactone but rather a conjugated C=O absorption. The nmr spectrum revealed only one single peak at 2.81 ppm and the uv spectrum indicated the retention of a quinoid structure. The elemental analysis gave an empirical formula as $C_5H_6O_2S$ and the mass spectral analysis gave its molecular weight as 260 (hence the correct molecular formula is $C_{10}H_{12}O_4S_2$) with a major fragmentation at 62. The compound decomposed at high temperature with the liberation of an intense odor of Me_2S (*m/e* 62). Based on these data the structure of this product is proposed as *p*-benzo-


VIIa, R = C_6H_5
b, R = H


VIII

quinone-2,5-dimethylsulfonium 3,6-dioxide[24] (VIII). Formation of sulfur ylides of this type has recently been reported.[25]

Biological Activity.—All compounds listed in Table I were screened by the CCNSC according to their protocols. Screening results of substituted *p*-benzoquinones having T/C values for leukemia L-1210 of more than 1.25 and/or T/C values for Walker carcinosarcoma 256 of less than 0.50 are listed in Table II. In spite of the fact that polyporic acid was reported to have significant and reproducible inhibitory activity against leukemia L-1210,[12,14a] this compound failed to show similar activity against leukemia L-1210 in the CCNSC test system.[26] This discrepancy was attributed to the difference in the type of mouse used in these experi-

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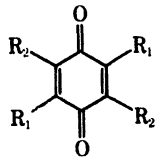
(24) The *Chemical Abstracts* name for this compound is sulfonium, (3,6-dihydroxy-*p*-benzoquinone-2,5-ylene)-bisdimethyl-, dihydroxide, bis-(inner salt).

(25) R. Gompper and H. Euchner, *Chem. Ber.*, **99**, 527 (1966).

(26) Test results were provided by contract screeners of CCNSC.

TABLE I

p-BENZOQUINONES



R_1	R_2	Mp, °C	Yield, %	Uv spectra λ_{max}^{EtOH}, mμ	log ε
OH	C_6H_5	315–317[a]	88	262	4.37
				320	3.97
OH	*p*-$CH_3C_6H_4$	294–296[b]	89	265	4.34
				330	3.73
OH	*p*-$C_2H_5C_6H_4$	262–264	78	264	4.38
				335	3.74
OH	*p*-$CH_3(CH_2)_3C_6H_4$	222–224	80	265	4.18
				312	3.51
OH	*p*-BrC_6H_4	311–312[c]	41	260	4.52
				310	4.11
OH	$CH_3(CH_2)_5$	155–156[d]	11	294	4.31
OCH_3	NH_2	258–260[e]	70	338	4.40
OCH_3	$CH_3(CH_2)_6NH$	95–97	94	226	4.44
				356	4.42
OCH_3	$CH_3(CH_2)_{13}NH$	78–80	96	226	4.35
				357	4.32
OCH_3	$CH_3(CH_2)_{14}NH$	90–92	96	226	4.49
				356	4.46
OCH_3	3,4-$(CH_3O)_2C_6H_3$-$(CH_2)_2NH$	193–195	100	227	4.61
				276	3.87
				359	4.35
OCH_3	3,4-$(CH_2O_2)C_6H_3$-CH_2NH	183–185	100	230	4.46
				283	3.93
				357	4.36
CH_3	NH_2	310–312	79	331	4.40
CH_3	$CH_3(CH_2)_5NH$	98–100	72	220	4.42
				3[illegible]	4.42
CH_3	$CH_3(CH_2)_6NH$	95–97	99	222	4.36
				347	4.40
CH_3	$CH_3(CH_2)_{13}NH$	87–89	84	222	4.36
				349	4.37
CH_3	$CH_3(CH_2)_{14}NH$	99–101	100	222	4.35
				348	4.34
C_6H_5	NH_2	326–328	95	279	4.00
				339	4.10
C_6H_5	$CH_3(CH_2)_5NH$	165–167	83	273	4.08
				351	4.36
C_6H_5	$CH_3(CH_2)_6NH$	144–145	90	272	4.12
				350	4.40
C_6H_5	$(CH_2)_5N$	220–222	75	237	4.29
				282	4.05
				430	3.84
N_3	H	93–95[f]	84	240	4.19
				325	4.35
N_3	CH_3	130–132	90	253	4.11
				325	4.24
N_3	CH_3O	115–116	51	264	4.26
				334	4.21
N_3	C_6H_5	118–120	81	247	4.35
				355	3.94
F	CH_3O	155–157	35	283	4.25
Cl	CH_3O	125–127	70	298	4.14
Cl	C_2H_5O	103–105[g]	65	297	4.20
Cl	$C_6H_5CH_2O$	144–146[h]	49	297	4.15
Cl	C_6H_5	207–209[i]	40	233	4.42
				263	4.13
				294	4.12
				332	3.70
Cl	*p*-$CH_3C_6H_4$	288–290[j]	36	240	4.46
				295	3.96
				370	3.96

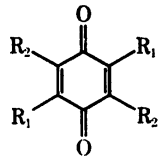
TABLE I (*Continued*)

R_1	R_2	Mp, °C	Yield, %	Uv spectra λ_{max}^{EtOH}, mμ	log ε
Cl	p-$C_2H_5C_6H_4$	267–269	30	241	4.35
				275	3.61
				370	3.61
Cl	p-$CH_3(CH_2)_3C_6H_4$	169–170	25	242	4.38
				298	3.49
				370	3.65
Cl	p-BrC_6H_4	302–304[k]	26	250	4.47
				276	4.22
				374	3.69
Br	CH_3	173–175[l]	86	288	4.30
Br	C_6H_5	227–229[a,m]	54	288	4.10
O^-	$(CH_3)_2S^+$	>330 dec	40	278	4.36
				291	4.36

[a] P. R. Shildneck and R. Adams, *J. Amer. Chem. Soc.*, **53**, 2373 (1931). [b] Reference 14b. [c] Reference 14b, mp 311° dec. [d] Reference 19, mp 154°. [e] Reference 16, mp 256°. [f] Exploded at 115°. [g] A. Oliverio and G. Werber, *Ann. Chim.* (Rome), **42**, 145 (1952), mp 104–105. [h] C. L. Jackson and G. Oenslager, *Am. Chem. J.*, **18**, 1 (1896), mp 142°. [i] D. E. Kealnes, *J. Amer. Chem. Soc.*, **56**, 2478 (1934), mp 208–209°. [j] Reference 14b. [k] Reference 14b, mp 304°. [l] A quinhydrone. [m] Mp 224°.

TABLE II

ANTITUMOR SCREENING RESULTS OF SEVERAL *p*-BENZOQUINONE DERIVATIVES



		Screening results							
		L-1210				WM-256			
R_1	R_2	Dose, mg/kg	Survival	Wt dif	T/C	Dose, mg/kg	Survival	Wt dif	T/C
OH	p-$C_2H_5C_6H_4$	400	1/4	−4.4	1.15	90	10/14	24	0.38
		200	4/4	−4.3	1.03	45	5/6	1	0.59
		150	3/4	−5.8	1.47				
		100	8/8	−3.8	1.37				
		65	4/4	−1.7	0.96				
N_3	CH_3O	80	0/6			60	0/6		
		40	3/6	−6.2		30	9/12	−13	0.37
		20	6/6	−2.3	0.98	15	12/12	−5	0.64
						7.5	12/12	−2	1.01
Cl	CH_3O	80	0/6			20	10/12	−9	0.45
		40	4/6	−2.5	1.01				
		20	6/6	−2.3	1.06				
Cl	C_6H_5	400	1/6	−2.9	0.75	800	0/6		
		200	6/6	−0.3	0.88	720	4/6	−22	0.31
						340	25/25	−14	0.51
						200	5/6	−15	0.28
						170	6/6	−13	0.60
						100	4/6	−3	0.64
						85	6/6	−12	1.20

ments (DBA *vs.* C_3H/DBA hydride).[27] It is of interest to note that an analog of polyporic acid, 2,5-dichloro-3,6-diphenyl-*p*-benzoquinone (IV, R = C_6H_5; X = Cl), displayed inhibitory activity against Walker 256 in rats[26] and a homolog of polyporic acid, 2,5-bis(*p*-ethylphenyl)-3,6-dihydroxy-*p*-benzoquinone (I, R = *p*-C_2H_5-C_6H_4), exhibited anticancer activity against leukemia L-1210 (the test system has been an early treated intraperitoneal L-1210 system with intraperitoneal drug administration) and Walker 256.[26] Inhibitory activity of 2,5-diazido-3,6-dimethoxy-*p*-benzoquinone (III, R = CH_3O) against Walker 256 was also observed.[26] The azido and halogenated derivatives are in general rather toxic [the lethal doses for 2,5-diazido-*p*-benzoquinone (III, R = H) and 2,5-difluoro-3,6-dimethoxy-*p*-benzoquinone (IV, X = F; R = CH_3O) are *ca.* 10 mg/kg]. None of the aminoquinones (II) displayed significant antitumor activity against leukemia L-1210. The pulvinic acid dilactone (VIIa) was found to be without antileukemic activity. *p*-Benzoquinone-2,5-dimethylsulfonium 3,6-dioxide (VIII) did not exhibit activity against WA-256. Severe body weight loss was noted with many of the aforementioned compounds that displayed activity against WA-256 as well as leukemia L-1210.

(27) Dr. Betty J. Abbott of CCNSC. Private communication.

Experimental Section[28]

2,5-Diazido-*p*-xyloquinone (III, R = CH_3).—To a stirred solution of 12 g (0.041 mol) of 2,5-dibromo-*p*-xyloquinone[29] in 300 ml of Me_2CO was slowly added, with cooling, an aqueous solution of activated NaN_3[30] [5.9 g (0.09 mol) in 150 ml of H_2O]. A brown solution was initially formed. Upon continuous stirring at room temperature an orange solid gradually precipitated. After 20 hr the solid was collected by filtration, washed (H_2O, 2 times with 50 ml), then vacuum dried to give 8.1 g (90% yield) of product, mp 130–132°.

Other azidoquinones were prepared by essentially the same procedure, reaction time, 4–20 hr (see Table I).

2,5-Diamino-3,6-dimethoxy-*p*-benzoquinone (II, R = CH_3O, R′ = H).—A fine suspension of 0.7 g of 2,5-diazo-3,6-dimethoxy-*p*-benzoquinone and 40 mg of PtO_2 in 250 ml of MeOH was hydrogenated at room temperature under 4.2 kg/cm² of H_2 for 90 min. The resulting mixture was filtered and the insoluble solid was extracted with 600 ml of boiling MeOH. The extract and the colorless filtrate (which turned purple on contact with air) were combined and concentrated *in vacuo* to *ca.* 10 ml. Upon cooling, 0.5 g (90% yield) of 2,5-diamino-3,6-dimethoxy-*p*-benzoquinone was obtained as dark purple crystals, mp 258–260°. The uv and ir absorption spectra of this product were found to be identical with those prepared by the treatment of tetramethoxy-*p*-benzoquinone with NH_3.[16]

Preparation of other diaminoquinones was carried out by essentially the same procedure (see Table I).

General Preparation of 2,5-Bis(alkylamino)-*p*-xyloquinones (II, R = CH_3).—A solution of 2.72 g (0.02 mol) of *p*-xyloquinone and 0.04 mol of the appropriate amine in 120 ml of EtOH was refluxed on a steam bath for 5 min. On cooling, the resulting purple crystals were collected by filtration and washed twice with 20 ml of EtOH and twice with 20 ml of petroleum ether. The crude product could be purified by recrystallization from EtOH (see Table I).

2,5-Bis(alkylamino)-3,6-dimethoxy-*p*-benzoquinones (II, R = OCH_3) were prepared by essentially the same procedure except that tetramethoxy-*p*-benzoquinone was used in place of *p*-xyloquinone.

2,5-Bis(*p*-ethylphenyl)-3,6-dichloro-*p*-benzoquinone (IV, X = Cl, R = *p*-C_2H_5-C_6H_4).—To a solution of 28.5 g (0.16 mol) of 2,5-dichloro-*p*-benzoquinone in 800 ml of MeOH and 280 ml of Et_2O was slowly and simultaneously added a diazotized mixture of *p*-ethylaniline [prepared by the addition of 28 g (0.41 mol) of $NaNO_2$ in 100 ml of H_2O to 44 g (0.36 mol) of *p*-ethylaniline in a solution of 100 ml of H_2O and 108 ml of concentrated HCl at 0°] and an aqueous solution of 72 g of NaOAc in 120 ml of H_2O. The addition took *ca.* 40 min. The reaction mixture was stirred at room temperature for 20 hr after which the solvent was evaporated under reduced pressure. The resulting residue was poured, with stirring, into 500 ml of H_2O. The brown solid was collected by filtration and extracted with 1 l. of warm (50–60°) EtOH. The orange solid, 20.3 g, mp 260°, was recrystallized from BuOH to give 18.5 g (30% yield) of pure product, mp 267–269°.

Analogous compounds were prepared by essentially the same procedure (see Table I).

2,5-Bis(*p*-ethylphenyl)-3,6-dihydroxy-*p*-benzoquinone (I, R = *p*-$C_2H_5C_6H_4$).—To a suspension of 5 g of 2,5-bis(*p*-ethylphenyl)-3,6-dichloro-*p*-benzoquinone in 50 ml of MeOH was added 100 ml of 10% NaOH. The mixture was stirred and refluxed for 10 min. The purple solution was filtered from any insoluble solid, and the filtrate was diluted with 50 ml of H_2O, and, with cooling, was acidified to pH 1 with HCl. The resulting brown solid was collected by filtration and dried to give 4.7 g of crude product, mp 255–258°. Recrystallization from toluene gave 3.5 g (78% yield) of pure product, mp 262–264°.

Other compounds in this series were prepared by essentially the same procedure (see Table I). The 2,5-bis(*p*-bromophenyl) analog was recrystallized from pyridine.

2,5-Dihexyl-3,6-dihydroxy-*p*-benzoquinone (I, R = $(CH_2)_5$-CH_3).—A mixture of 65 g (0.5 mol) of heptanoic acid and 119 g of $SOCl_2$ in 200 ml of $CHCl_3$ was refluxed for 1 hr. The solvent was removed under reduced pressure and the residual syrup was diluted with 300 ml of petroleum ether. The mixture was filtered and the filtrate evaporated to give 73 g of residue. This was dissolved in 300 ml of pentane and added dropwise to a mixture of 78 g of Na_2O_2, 500 g of crushed ice, and 500 ml of cold H_2O. The temperature was maintained between 0 and 5°. After the addition was complete, the mixture was stirred for an additional 20 min. The aqueous layer was extracted twice with 600 ml of pentane. The combined pentane solutions were washed with a small amount of cold H_2O and dried (Na_2SO_4). The solvent was then evaporated at room temperature *in vacuo* to give 54 g of the acyl peroxide.

To a warm (90°) suspension of 10 g of 2,5-dihydroxy-*p*-benzoquinone in 350 ml of AcOH was slowly (15 min) added the aforementioned heptanoyl peroxide with stirring. The temperature of the reaction mixture was kept at 90° for 30 min with continued stirring and then was allowed to stir overnight at room temperature. The orange crystals which separated were collected by filtration to give 5 g of crude product, mp 150–155°. Recrystallization from EtOH–H_2O gave 2.3 g (11% yield) of pure product as fine, orange-red needles, mp 155–156°.

***p*-Benzoquinone-2,5-dimethylsulfonium 3,6-Dioxide (VIII).**—A mixture of 2.8 g (0.02 mol) of 2,5-dihydroxy-*p*-benzoquinone in 50 ml of DMSO and 25 ml of Ac_2O was heated on a water bath (60°) for 3 min. The reaction mixture was then allowed to cool overnight. The resulting solid was collected by filtration and washed successively with 5 ml of Ac_2O, twice with 20 ml of C_6H_6, and twice with 20 ml of petroleum ether to give 2.2 g (42% yield) of yellow solid, mp >360° (darkened at 330°). Recrystallization from 60 ml of AcOH gave 55% recovery of yellow needles, mp >360° (darkened at 330°). The product was very soluble in H_2O, soluble in hot AcOH, slightly soluble in EtOH, 2-ethoxyethanol, and BuOH, and insoluble in pyridine and C_6H_6. Its nmr spectrum in CF_3CO_2H showed only a single peak at 2.81 ppm (TMS). The ir showed neither OH nor unsaturated γ-lactone absorption (as in the case of compound VII). The uv still retained the quinone absorption spectrum [λ_{max}^{EtOH} 278 mμ (log ε 4.36), 291 mμ (log ε 4.36); λ_{sh}^{EtOH} 300 mμ (log ε 4.30)]. The product liberated Me_2S (*m/e* 62) and a trace of DMSO on heating (verified by mass spectrum determination). Its molecular weight was 260 (mass spectrum).

Anal. ($C_{10}H_{12}O_6S_2$) C, 46.14; H, 4.65; S, 24.63. Found: C, 45.94; H, 4.62; S, 24.83.

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(28) All melting points (corrected) were taken on a Thomas–Hoover melting point apparatus. The uv absorption spectra were determined with a Beckman DK-2 spectrophotometer. Where analyses are indicated only by symbols of the elements, analytical results obtained for those elements were within ±0.4% of the theoretical values.

(29) L. I. Smith and J. Nichols, *J. Amer. Chem. Soc.*, **65**, 1739 (1943).

(30) Activated NaN_3 can be prepared by a modified procedure of P. A. S. Smith [*Org. React.*, **3**, 382 (1964)]: in 200 ml of $(H_2N)_2$, 58 g of commercial NaN_3 was dissolved. The resulting soln was filtered from insoluble material, and to the filtrate was added slowly, with cooling, 400 ml of Me_2CO. The resulting precipitate was collected by filtration, washed twice with 150 ml of Me_2CO, and dried *in vacuo*, yield 38 g.