Preparation of 2,5-Bis(alkylamino)-3,6-dimethoxy-*p*-benzoquinones

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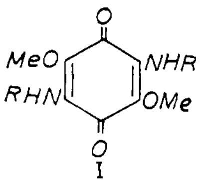
The properties and method of preparation of several 2,5-bis(alkylamino)-3,6-dimethoxy-*p*-benzoquinones are described.

REACTION of tetramethoxyquinone with primary amines yielded 2,5-bis(alkylamino)-3,6-dimethoxy-*p*-benzoquinones of general formula I. The scope of the reaction has been previously discussed (*2*). Table I summarizes the preparation and properties of several other members of this series. The reactions proceeded smoothly in methanol at reflux temperature. Approximately 30 ml. of methanol per gram of tetramethoxyquinone was used. Usually a ratio of 4 moles of amine to 1 mole of tetramethoxyquinone was sufficient to produce complete reaction. Purity of the compounds was established by thin-layer chromatography and by elemental analysis. The compounds moved as a single spot on silica, and their analysis was within the acceptable range.



I

The auxochromic effect of amino groups, which deepens the color of these quinones, has been commented on in detail elsewhere (*1*, *3*). Ultraviolet absorption maxima of quinones derived from aromatic amines occur at longer wavelength than the maxima of quinones derived from aliphatic amines. The spectra of the aliphatic aminoquinones show absorptions at 220 mμ(ϵ = 25,000) and 369 mμ(ϵ = 20,000), while the spectra of the aromatic aminoquinones show absorptions at 260 mμ(ϵ = 25,000) and 400 mμ(ϵ = 17,000). The infrared spectra of these and related compounds (*1*, *2*) show absorption at 3.0 microns (N—H) and at 6.1 and 6.4 microns (quinone). Infrared spectra were obtained on a Perkin-Elmer Infracord, Model 137; ultraviolet spectra were obtained on a Bausch and Lomb Spectronic 505.

Table I. Characterization of 2,5-Bis(alkylamino)-3,6-dimethoxy-*p*-benzoquinones

Amine	M.P., °C.	Formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H	Color	Reflux, Hr.	Crystal. Solvent	Yield, %
Furfuryl	147	$C_{18}H_{18}N_2O_6$	60.3	5.1	60.2	5.2	Black	10	EtOH	78
Cyclohexyl	165–190[a]	$C_{20}H_{30}N_2O_4$	66.3	8.3	66.2	8.4	Green	1	EtOH	90
Benzyl	213	$C_{22}H_{22}N_2O_4$	69.8	5.9	69.5	6.0	Black	0.1	$CHCl_3$	90
α-Phenylethyl	183	$C_{24}H_{26}N_2O_4$	70.9	6.4	70.9	6.5	Black	21	Acetone	88
β-Phenylethyl	192	$C_{24}H_{26}N_2O_4$	70.9	6.4	70.7	6.4	Violet	0.3	C_6H_6	92
o-Toluidine	235	$C_{22}H_{22}N_2O_4$	69.8	5.9	69.8	5.9	Green	144	EtOH	14
m-Toluidine	250	$C_{22}H_{22}N_2O_4$	69.8	5.9	69.7	5.7	Black	20	CH_2Cl_2	85
o-Ethylaniline	196	$C_{24}H_{26}N_2O_4$	70.9	6.4	70.8	6.6	Green	117	EtOH	11
p-Ethylaniline	203	$C_{24}H_{26}N_2O_4$	70.9	6.4	71.0	6.6	Green	21	EtOH	86
o-Phenetidine	183	$C_{24}H_{26}N_2O_6$	65.7	6.0	65.9	6.0	Black	53	EtOH	50
p-Phenetidine	263	$C_{24}H_{26}N_2O_6$	65.7	6.0	65.5	5.8	Black	15	Dioxane	93
2,3-Dimethylaniline	254	$C_{24}H_{26}N_2O_4$	70.9	6.4	71.1	6.5	Green	87	C_6H_6	18

[a] Decomposes.

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Tetrachloroethyl and Trichlorovinyl Thiolsulfonate Esters

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Trichlorovinyl and tetrachloroethyl thiolsulfonates have been prepared by treating sodium and zinc sulfinates with tetrachloroethanesulfenyl chloride. The resulting compounds are generally mixtures of the trichlorovinyl and tetrachloroethyl forms and are purified with difficulty by thin-layer chromatography. Infrared and NMR spectra are given.

TRICHLOROMETHYL thiolsulfonates (*1*, *2*) are the only thiolsulfonate esters that have been reported with halogen substitution in the *S*-alkyl grouping. Tetrachloroethanesulfenyl chloride was shown to react with various nucleophiles—e.g., sodium phthalimide and sodium cyanide (*3*)—and has been employed here to produce new halogen-substituted *S*-alkyl thiolsulfonates.

In the above report (*3*) of the reaction of tetrachloroethanesulfenyl chloride with salts of phthalimide or tetrahydrophthalimide, it was noted that *N*-trichlorovinylthioimides were unexpectedly produced. Dehydrochlorination was said to occur simultaneously or consecutively with replacement of the chlorine on the sulfur. The present paper discusses reaction of the sulfenyl chloride with some metal sulfinates, mostly zinc, illustrated by the following equations:

$$2ClSCHClCCl_3 + [RS(O)\,O]_2Zn \rightarrow 2RSO_2SCHClCCl_3 + ZnCl_2$$

$$2RSO_2SCHClCCl_3 \rightarrow 2RSO_2SCCl{=}CCl_2 + 2HCl$$

Initial analyses of the products of the reaction of alkyl sulfinates with tetrachloroethanesulfenyl chloride indicated that they were mixtures of the *S*-tetrachloroethyl and *S*-trichlorovinyl derivatives. Repeated purification using thin-layer chromatography gave the pure trichlorovinyl alkyl esters.

A number of aromatic sulfinates were treated with tetrachloroethanesulfenyl chloride but only the phenyl, *p*-bromobenzene, and *p*-chlorobenzene compounds were obtained in pure form. The first reaction between sodium benzenesulfinate and the sulfenyl chloride yielded a crystalline product, the elemental analysis of which gave results comparing favorably with the percentages calculated for the trichlorovinyl structure. Subsequent reactions between the sodium salt or the zinc salt and the sulfenyl chloride formed oily products from which crystalline substances could be isolated only by thin-layer chromatography. In all cases these analyzed for the trichlorovinyl structure. Reactions of zinc *p*-bromobenzenesulfinate and zinc *p*-chlorobenzenesulfinate with the sulfenyl chloride, however, gave crystalline products which analysis showed were the tetrachloroethyl derivatives.

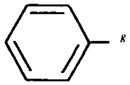
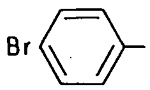
Since the unsubstituted phenyl compound had crystallized only in the unsaturated form (and only this form was isolable by chromatography), the authors thought that the *p*-bromo and *p*-chloro compounds might be dehydrochlorinated on silica by TLC to give the trichlorovinyl structures. Chromatography of pure tetrachloroethyl *p*-chlorobenzenethiolsulfonate gave only one discrete band, which upon isolation proved to be a small amount of starting material, and a diffuse yellow area beneath, apparently various decomposition products. Repeated attempts to make the trichlorovinyl compound gave only decomposition products. In other experiments ammonia was bubbled through acetone or benzene solutions of tetrachloroethyl *p*-chlorobenzenethiolsulfonate, but the only material that could be recovered and identified was ammonium chloride.

In an attempt to measure the relative amounts of the *S*-trichlorovinyl and *S*-tetrachloroethyl products the compounds were analyzed by nuclear magnetic resonance. The results of these analyses showed the crystalline phenyl derivative to be pure trichlorovinyl benzenethiolsulfonate, the aliphatic compounds less pure trichlorovinyl thiolsulfonates, and the *p*-chlorophenyl product pure tetrachloroethyl *p*-chlorobenzenethiolsulfonate. The spectrum of the reagent, tetrachloroethanesulfenyl chloride showed 5 to 10% of an impurity, possibly the isomer, 1,1,2,2-tetrachloroethanesulfenyl chloride, but its reaction product with sodium benzenesulfinate gave a complicated spectrum. NMR results for the compounds are included in detail in Tables I and II.

EXPERIMENTAL

Purified zinc sulfinates were prepared by treating the commercially available sulfonyl chlorides with zinc and recrystallizing the products from water or alcohol. Sodium benzenesulfinate was obtained from the Eastman Kodak Co. The dried sulfinate was either dissolved or suspended in *N,N*-dimethylformamide, depending on solubility, the mixture cooled to 15° C., and tetrachloroethanesulfenyl chloride added dropwise (supplied by Hooker Chemical Co.;

Table I. Trichlorovinyl Thiolsulfonates, $RSO_2SCCl = CCl_2$[a]

R	n_D^{20}	Infrared Absorption (SO_2) Cm.$^{-1}$		NMR[b] CH_3—	—CH_2—	—CHCl[c]—	Other	Calculated Formulas	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found	Sulfur, % Calcd.	Sulfur, % Found
CH_3—	1.5634	1142[d]	1339[e]	6.54				$C_3H_3Cl_3O_2S_2$	14.90	15.18	1.25	1.52	44.03	44.60	26.54	26.90
C_2H_5—	1.5636	1132[d]	1340[e]	8.50	6.41	3.94	3.25 Olefinic H	$C_4H_5Cl_3O_2S_2$	18.79	18.46	1.97	2.15	41.61	41.52	25.09	25.40
n-C_3H_7—	1.5552	1135[d]	1340[e]	8.87	8.01 6.53[f]	4.00	3.30 Olefinic H	$C_5H_7Cl_3O_2S_2$	22.27	21.73	2.61	2.91	39.45	39.65	23.78	23.50
n-C_4H_9—	1.5598	1140[d]	1341[e]	9.00	8.30 6.53[f]	3.98		$C_6H_9Cl_3O_2S_2$	25.40	25.71	3.19	3.26	37.49	37.30	22.60	23.70
 [g]		1150[d]	1340[e]				2.24 phenyl	$C_8H_5Cl_3O_2S_2$	31.64	31.97	1.65	1.61	34.03	34.90	21.12	20.80
 [h]		1155[d]	1350[e]				2.27 phenyl	$C_8H_4BrCl_3O_2S_2$	25.12	25.51	1.05	1.26	27.82	27.80	16.76	17.11

[a] Analyses performed by Weiler and Strauss, Microanalytical Laboratories, Oxford, England. [b] TMS internal reference (τ values given). [c] These peaks can be ascribed to small amounts of the undehydrochlorinated form. Source of olefinic hydrogen is unknown. [d] *Sym*, S-O. [e] *Asym*, S-O. [f] CH_2 groups adjacent to - SO_2. [g] M.p. 85–6° C. (not corrected). [h] Not crystallizable.

Table II. Tetrachloroethyl Thiolsulfonates, $RSO_2SCHClCCl_3$[a]

R	M.P., °C.	Infrared Absorption (SO_2) Cm.$^{-1}$ [c,d]		NMR[b]		Calculated Formulas	Carbon, %		Hydrogen, %		Chlorine, %		Sulfur, %	
				Phenyl	CHCl		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
	89-90	1135[c]	1330[d]	2.04 2.38	4.04	$C_8H_5Cl_5O_2S_2$	25.65	25.98 25.76[e]	1.34	1.51 1.46[e]	47.33	48.00 47.40[e]	17.12	16.49 17.09[e]
 [f]	84-86	1140[c]	1338[d]			$C_8H_5BrCl_4O_2S_2$	22.93	23.63	1.20	1.24	42.31	40.04	15.30	15.26

[a] Melting points uncorrected. Analyses, except[e], by Weiler & Strauss. [b] TMS internal reference (τ values given). [c] *Sym*, S–O. [d] *Asym*, S–O. [e] Analyzed by Galbraith Laboratories, Knoxville, Tenn. [f] Not enough for NMR analysis.

analysis by NMR indicated a mixture of 85% 1,2,2,2-tetrachloroethanesulfenyl chloride and 15% of the 1,1,2,2-tetrachloroethyl isomer). Water was then added to the mixture and the light yellow organic product separated. The aliphatic compounds were diluted with ether and dried over sodium sulfate before chromatographing. The aromatic compounds, which did not crystallize from the oil, were handled similarly.

The compounds, which were purified by thin-layer chromatography, were applied in about 5% ether solution to plates coated to a thickness of 250 microns with silica gel GF_{254} (Merck) containing a fluorescent indicator, and were developed in benzene, or benzene-petroleum ether (30 to 60° C.)-chloroform, 8:8:1 by volume.

The NMR data were obtained on a Varian DP-60 nuclear magnetic resonance spectrometer. Chemical shifts were determined by side bands applied with an audio-oscillator for which the frequency is continuously monitored by an electronic counter. The samples were run in a concentration of 20 to 40% by volume in carbon tetrachloride at a temperature of approximately 33° C.

The infrared spectra were obtained on a Beckman IR-4 spectrophotometer using sodium chloride optics. The liquid samples were run neat and the solids in Nujol mulls.

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Synthesis of 1,2,3,4,9,9-Hexachloro-1,4,4a,5,6,7,8,8a-octahydro-1,4-methanonaphthalene-6,7-dicarboxylic Acid and Ester Derivatives

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The reaction of 4-cyclohexene-1,2-dicarboxylic anhydride (I) with hexachlorocyclopentadiene under Diels-Alder conditions gives rise to two stereoisomeric adducts. Both isomers, II-m.p. 278–280° C. and III-m.p. 256–257.5° C., are reactive with hydroxyl compounds in the formation of mono- and diesters.

THE CHEMISTRY of hexachlorocyclopentadiene has been reviewed (*2*, *3*). Of particular interest have been the various products from the Diels-Alder reaction with unsaturated dicarboxylic acids or their anhydrides. This paper reports the Diels-Alder reaction of hexachlorocyclopentadiene with 4-cyclohexene-1,2-dicarboxylic anhydride (I).

EXPERIMENTAL

Preparation of Isomeric 1,2,3,4,9,9-Hexachloro-1,4,4a,5,6,7,8,8a-octahydro- 1,4-methanonaphthalene-6,7-dicarboxylic Anhydrides. In a 3-liter, three-necked, round-bottomed resin kettle equipped with a reflux condenser, stirrer, thermometer, nitrogen inlet tube, and heating mantle (controlled with a Honeywell Brown Pyr-O-Vane) was placed 456 grams (3 moles) of *cis*-4-cyclohexene-1,2-dicarboxylic anhydride (Allied Chemical Corp.), 816 grams (3 moles) of hexachlorocyclopentadiene (Hooker Chemical Co.), and 320 grams (25% based on reactants) of mixed xylenes. The mantle temperature was maintained at 210° C., and the reaction temperature 173° C. at its highest, dropped to 159° C. during 16 hours. The reaction mixture was cooled to 110° C., treated with 300 ml. of mixed xylenes, and equilibrated at 110° C. for 4 hours; the solid product was isolated by suction filtration through a steam jacketed Büchner funnel. The filter cake was washed with two 100-ml. portions of hot (100° C.) mixed xylenes and then with two 100-ml. portions of *n*-heptane. The crude product was dried under vacuum at 110° C. for 16 hours to give 1000 grams (78.4%), m.p. 240° C., of isomeric adducts. Recrystallization from 4000 ml. of 1,2-dibromoethane gave 791 grams (62%) of a high melting isomer (compound II), m.p. 278° C. Distillation of the filtrate to a volume of 500 ml. gave 150 grams (11.8%) of a mixture of high and low melting isomers. Repeated recrystallization of this mixture of isomers from toluene-butanone resulted in the isolation of the pure low melting material (compound III), m.p. 256–