6.5 ml. of a 4.5M solution of sodium methoxide in methanol was added. A precipitate of colorless plates formed immediately. The mixture was shaken once and allowed to stand for 1 hr. at room temperature. It was then added, still under nitrogen, to 100 ml. of water which had been boiled and allowed to cool under nitrogen. The solution was neutralized by dropwise addition of acetic acid and the precipitate of long faintly blue needles was filtered off, washed with cold water, and dried under vacuum, yielding 1.24 g. (68%) of (trimethylsilyl)hydroquinone, m.p. 126–127°. Recrystallization from n-hexane removed the blue color but did not change the melting point.

Anal. Calcd. for $C_9H_{14}O_2Si$: C, 59.3; H, 7.7; Si, 15.4. Found: C, 59.7; H, 8.0; Si, 15.4.

In two other experiments, using 2M sodium methoxide solution and reaction times of 1 hr. and 18 hr. the yields of (trimethylsilyl)hydroquinone were 33% and 48%. It is essential that the reaction mixture be protected from air at all times until after the neutralization has been completed. Traces of oxygen cause the development of a deep black color and reduce the yield and purity of the product.

4-(Trimethylsilyl)catechol. A mixture of 3.26 g. (0.01 mole) of 3,4-bis(trimethylsiloxy)trimethylsilylbenzene and 6.5 ml. of 4.5M sodium methoxide solution was allowed to stand under nitrogen at room temperature for 5 min. and was then diluted with 100 ml. of deaerated water and neutralized with acetic acid as in the preceding example. A brown oil separated which was extracted with 100 ml. of diethyl ether. The extract was washed several times with water to remove any catechol which might have been produced and was then dried over sodium sulfate. After evaporation of the ether there remained 1.6 g. of dark brown oil which partially solidified on standing at 0°. The oil was dissolved in 20 ml. of pentane, treated with decolorizing carbon and the pentane solution was cooled to −20°. The colorless plates which separated were filtered off, washed with cold pentane, and dried under vacuum. The yield of purified 4-(trimethylsilyl)catechol was 0.62 g. (34%); m.p. 33–35°.

Anal. Calcd. for $C_9H_{14}O_2Si$: C, 59.3; H, 7.7; Si, 15.4. Found: C, 59.7; H, 7.9; Si, 14.8.

When the reaction was carried out using a 2M sodium methoxide solution and a reaction time of 18 hr., the only product isolated was catechol, obtained in 54% yield. The desired compound was obtained, along with some catechol, when the aryloxysilane reacted for 1 hr. with 2M sodium methoxide or 15 min. with a 4.5M solution, but the product was contaminated with an unidentified compound which could not be completely removed by crystallization from pentane and which resulted in slightly low silicon and carbon analyses.

Attempted preparation of 4-(trimethylsilyl)resorcinol. Several attempts were made to convert 2,4-bis(trimethylsiloxy)trimethylsilylbenzene to (trimethylsilyl)resorcinol, varying the sodium methoxide concentration, reaction time, and temperature. In every case the aqueous solution appeared completely homogeneous and the only product which could be isolated by extraction was resorcinol, which was obtained in over 80% of the theoretical amount.

(Trimethylsilyl)benzoquinone-1,4. A solution of 1 g. of (trimethylsilyl)hydroquinone in 60 ml. of diethyl ether was stirred for 2 hr. with 5 g. of silver oxide and 5 g. of anhydrous sodium sulfate.[6] The mixture was filtered and the ether evaporated under vacuum, leaving 0.62 g. of yellow solid melting at 60–65°. Vacuum sublimation of this material yielded bright yellow needles of (trimethylsilyl)benzoquinone-1,4; m.p. 67–68°.

Anal. Calcd. for $C_9H_{12}O_2Si$: C, 60.0; H, 6.7; Si, 15.6. Found: C, 59.8; H, 6.7; Si, 15.3.

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[6] L. F. Fieser, W. P. Campbell, and E. M. Fry, *J. Am. Chem. Soc.*, **61**, 2216 (1939).

Derivatives of 1-Thia-4,5-diazacyclohepta-2,4,6-triene. IV.[1] Systems Containing Chloro Substituents

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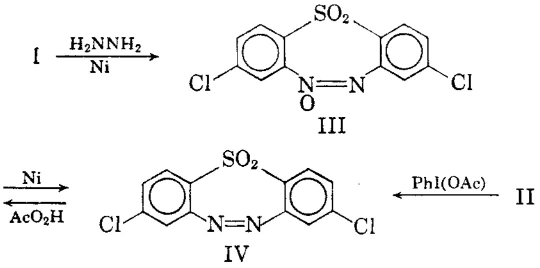
In continuation of the study of compounds derived from dibenzo-1-thia-4,5-diazacyclohepta-2,4,6-triene it was of interest to prepare derivatives containing chloro substituents. This purpose was achieved by the cyclization reactions of both di(4-chloro-2-nitrophenyl)sulfone (I) and di(4-chloro-2-aminophenyl)sulfone (II).

The reductive cyclization of I was accomplished most conveniently by the controlled reduction using hydrazine in the presence of Raney nickel, and in this fashion the cyclic azoxy compound (III) was obtained in 60% yield. The reductive cyclization of I by means of iron or zinc in acidic medium was less reliable. The reduction of I with an excess of hydrazine gave quantitative yields of the corresponding diamine II. The latter was subjected to the previously described[3] oxidative cyclization using iodosobenzene diacetate to give good yields of the cyclic azo compound IV. The new cyclic compounds were related chemically by the essentially quantitative oxidation of IV to III by means of peracetic acid, and by the reduction of III to IV using Raney nickel in diethyl carbitol in a manner analogous to a conventional desulfurization procedure.



From the reaction mixture of I, hydrazine, and Raney nickel, there was isolated on two separate occasions a product which, upon purification by chromatography on alumina, showed an analysis in accord with the structure of the nitrosohydroxylaminophenyl sulfone. This result is analogous to the previously described[1] o-nitrosophenyl o'-hydroxylaminophenyl sulfone, but unlike the latter, the compound described in this study could not be dehydrated to the cyclic azoxy compound.

Catalytic hydrogenation of I in the presence of Raney nickel gave a poor yield of the cyclic hydrazo

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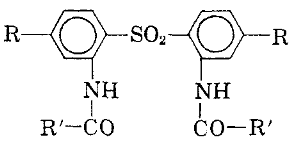
[1] For paper III see *J. Am. Chem. Soc.*, **79**, 5583 (1957).

[2] Present address: Department of Chemistry, University of Puerto Rico, Rio Piedras.

[3] H. H. Szmant *et al.*, *J. Am. Chem. Soc.*, **78**, 458 (1956); **79**, 4382 (1957).

TABLE I

New Derivatives of Di(o-aminophenyl) sulfone



R	R′	M.P.	Yield, %	Formula	Calcd., % C	H	S	N	Found, % C	H	S	N
H	H	205	80	$C_{14}H_{12}O_4N_2S$	55.26	3.98		9.21	55.33	3.93		9.39
H	CF_3	220[a]	82	$C_{16}H_{10}O_4N_2SF_6$	43.64	2.29	7.28	6.36	44.77	2.34	7.27	6.21
Cl	H	284[b]	67	$C_{14}H_{10}O_4N_2SCl_2$	45.06	2.70	8.59	7.50	45.68	2.68	8.73	7.39
Cl	CH_3	245	88[c]	$C_{16}H_{14}O_4N_2SCl_2$	47.88	3.51	7.98	6.98	47.76	3.46	7.99	6.56
Cl	CF_3	268	54	$C_{16}H_8O_4N_2SF_6Cl_2$	37.73	1.58	6.29	5.50	38.09	2.00	6.04	5.40

[a] % F, calcd. 25.89; found 25.33. [b] % Cl, calcd. 19.00; found 18.84. [c] This amide was obtained only when catalytic amounts of perchloric acid were added.

compound which was readily oxidized by air to a complex mixture of products including III.

For the synthesis of larger amounts of IV from II it was of interest to find an oxidizing agent more economical than iodosobenzene diacetate. Since di(o-aminophenyl)sulfone was cyclized by means of peracetic acid,[4] there was now investigated the use of 6% hydrogen peroxide in the presence of formic acid. Instead of an oxidation reaction there was produced the diformamide of II, while the use of hydrogen peroxide in trifluoroacetic acid gave the ditrifluoroacetamide. Since the use of acetic acid as solvent lead to no reaction whatsoever, it was suspected that the amide formation takes place only in the presence of relatively strong acids and in support of this assumption is the observation that the diacetamide of II was obtained in acetic acid when perchloric acid was also present. The parent compound, di(o-aminophenyl)sulfone, was converted in similar fashion to the corresponding diformamide and ditrifluoroacetamide.

The nitration of III gave a mononitro derivative which, on the basis of previous work,[5] is thought to contain the nitro group *para* to the oxygen-free azoxy nitrogen atom.

EXPERIMENTAL[6]

Di(2-amino-4-chlorophenyl)sulfone (II). A solution of 3.8 g. of di(2-nitro-4-chlorophenyl)sulfone (I) in 150 ml. of ethylene glycol was treated with 1.5 ml. of 95% hydrazine and a small amount of Raney nickel. The mixture was stirred for 24 hr. maintaining the temperature below 35° and then poured into water. Crystallization of the precipitate from ethanol gave a 97% yield of *II*, m.p. 165°.

Anal. Calcd. for $C_{12}H_{10}O_2Cl_2SN_2$: C, 45.45; H, 3.18; N, 8.83; S, 10.11. Found: C, 45.68; H, 3.11; N, 8.49; S, 9.78.

II was also prepared in 98% yield by the catalytic hydrogenation of I in the presence of Raney nickel in acetic acid and at an initial pressure of 42 p.s.i. The reduction of I in a mixture of benzene and water and using iron filings and catalytic amounts of hydrochloric acid gave only 36% of II.

Cyclization of I *to* III. A solution of 7.6 g. of I in Diethyl Carbitol was cooled in an ice bath and treated with 1.2 ml. of 95% hydrazine in the presence of a small amount of Raney nickel. The mixture was stirred for 24 hr., filtered, and the filtrate was concentrated at 80–85° (8 mm.). The residue was poured into water and the azoxy compound III was obtained in 60% yield, m.p. 245° upon crystallization from ethanol.

Anal. Calcd. for $C_{12}H_6O_3Cl_2SN_2$: C, 43.78; H, 1.84; S, 9.74; N, 8.51; Cl, 21.55. *Found:* C, 43.48; H, 1.89; S, 9.97; N, 8.47; Cl, 21.27.

A benzene solution of III was chromatographed on alumina (elution by benzene containing 10% methanol) and shown to be homogeneous.

Cyclization of II *to* IV. A mixture of 3.2 g. of II, 5.8 g. of iodosobenzene diacetate and 500 ml. of dry benzene was allowed to stand for 3 days at room temperature. The mixture was filtered to remove a small amount of precipitate, and the filtrate was subjected to steam distillation. The solid residue from the steam distillation was crystallized from isopropyl alcohol and benzene to give 71% of IV, m.p. 175°.

Anal. Calcd. for $C_{12}H_6O_2N_2SCl_2$: C, 46.02; H, 1.61; S, 10.24; N, 8.95; Cl, 22.65. Found: C, 46.20; H, 1.85; S, 10.31; N, 8.73; Cl, 22.46.

Oxidation of IV *to* III. A solution of 0.5 g. of IV in 45 ml. of acetic acid was treated with 10 ml. of 35% hydrogen peroxide, and after the initial reaction subsided, the mixture was refluxed for 24 hr. Upon cooling the solution deposited yellow crystals, m.p. 240°, which upon crystallization gave m.p. 245° and no depression of authentic III.

Reduction of III *to* IV. A solution of 0.5 g. of III in 50 ml. of Diethyl Carbitol was warmed with approximately 1 g. of Raney nickel. The mixture was filtered after 15 min. at 70–80°, and the filtrate was poured into water. The solid product was crystallized from benzene to give 0.2 g. of IV, m.p. 175°.

2-Nitroso-2′-hydroxylamino-4,4′-dichlorodiphenyl sulfone. A solution of 7.6 g. of I in 300 cc. of Diethyl Carbitol was treated with 1.2 ml. of 95% hydrazine in the presence of Raney nickel. The mixture was worked up as described above for the preparation of III. The product was chromatographed on alumina and elution with benzene gave 4.8 g. of III, while subsequent elution with methanol gave 0.7 g. of white crystals, m.p. 255°.

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(4) H. H. Szmant and Y. L. Chow, *J. Am. Chem. Soc.*, **79**, 4382 (1957).

(5) H. H. Szmant and Y. L. Chow, unpublished work and in part presented at the meeting of the American Chemical Society, San Francisco, 1958.

(6) The melting points are uncorrected. All microanalyses by Dr. Alfred Bernhardt, Mülheim, Ruhr, Germany.

Anal. Calcd. for $C_{12}H_8O_4Cl_2SN_2$: C, 41.54; H, 2.32; S, 9.23; N, 8.06; Cl, 20.42. Found: C, 41.50; H, 2.65; S, 8.95; N, 7.73; Cl, 20.25.

Reduction of I *to the cyclic hydrazo compound.* A solution of 23 g. of I in acetic acid was hydrogenated in the presence of Raney nickel at the initial pressure of 40 p.s.i. The mixture was filtered and diluted with water. The aqueous solution deposited yellow crystals which were chromatographed on alumina using a mixture of benzene–10% methanol for elution. There was isolated a 13% yield of yellowish crystals, m.p. 130°.

Anal. Calcd. for $C_{12}H_8O_2Cl_2SN_2$: C, 45.72; H, 2.24; N, 8.88; S, 10.17; Cl, 22.49. Found: C, 45.41; H, 2.30; N, 8.61; S, 10.09; Cl, 22.18.

Attempted oxidative cyclizations of II *with hydrogen peroxide.* The attempted oxidative cyclizations of II were carried out by dissolving the diamine in the organic acid, addition of an excess of 6% hydrogen peroxide and warming the reaction mixture for 24 hr. The products were isolated by pouring the mixture on ice and water, and crystallization of the solids from suitable solvents. The same procedure was employed with the parent compound di(*o*-aminophenyl)sulfone. The experimental results are summarized in Table I.

Mononitro derivative of III. A mixture of 10 ml. of nitric acid (sp. gr. 1.416) and 5 ml. of concd. sulfuric acid was added dropwise to an ice cold solution of 1 g. of III in 35 ml. of concd. sulfuric acid. The nitration mixture was kept in a refrigerator for 72 hr. and then poured on ice. The white solid was obtained in 60% yield and upon crystallization from benzene gave m.p. 264°.

Anal. Calcd. for $C_{12}H_5O_5Cl_2SN_3$: C, 38.50; H, 1.34; N, 11.23. Found: C, 38.25; H, 1.49; N, 11.67.

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Tetrahydroisoquinolinediones. I. The Structure of 4-Hydroxyisocarbostyril

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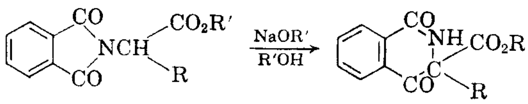
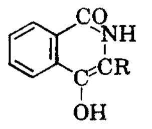
Received March 15, 1 61

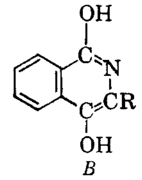
Over sixty years ago Gabriel and Colman[1] reported a base-catalyzed rearrangement of α-phthalimido esters to form derivatives of isoquinoline, hydrolysis and decarboxylation of which gave compounds that were reported as 4-hydroxy-3-alkylisocarbostyrils (structure *A*), as the result of evidence obtained by degradation. A similar rearrangement was observed with α-phthalimido ketones.[2] These reactions will hereafter be called the Gabriel-Colman rearrangement.



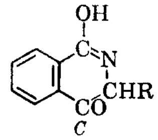
There are two points in structure *A* at which tautomerism is possible, permitting the possibility of three other structures, *B*, *C*, and *D*, in equilibrium with *A*. These possibilities cannot be ruled out on the basis of previously reported structural work.

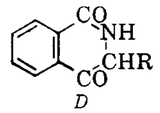
The bisenol structure *B* would appear to be the most likely structure because of its aromatic character. However, isoquinolone, in which the aromatic structure would seem even more likely, is a neutral compound whose ultraviolet absorption spectra are identical in acidic, basic, and neutral media.[3,4] This result would be possible only with an amide structure exhibiting very little tautomerism. Actually, the amide structures of isoquinolone and structure *A* are probably as aromatic as structure *B*, as the result of completion of the electronic requirements for aromaticity by the unshared pair of electrons on the nitrogen atom. Structures *B* and *C* thus appear to be less likely than *A* and *D*.


A


B

I. R = CO_2CH_3
II. R = H
III. R = CH_3


C


D

In order to make a more exact evaluation of the structures of the 4-hydroxyisocarbostyrils, the ultraviolet absorption spectra of three of these compounds have been compared with the spectra of 1,4-naphthoquinone and 1,4-dihydroxynaphthalene in neutral, basic, and acidic solutions. In structures *B* and *C* the nitrogen atom should show basic properties. However, no significant differences were observed in comparing the spectra of these compounds in acid solution with their spectra in neutral solution, indicating the absence of protonation. Structures *B* and *C* can therefore be eliminated.

In comparing the spectra of the neutral solutions (Fig. 1) with those of the basic solutions (Fig. 2), two assumptions can be made. First, compounds showing spectra closely resembling those of 1,4-naphthoquinone or 1,4-dihydroxynaphthalene will have electronic configurations similar to the configurations of these models, and should have about the same amounts of keto, enol, or enolate at both the 1,2- and the 3,4-locations. Second, for R = CO_2CH_3 (I), the extent of 3,4-enolization should be much greater than of 1,2-enolization as the result of hydrogen-bond stabilization of the 3,4-

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(1) S. Gabriel and J. Colman, *Ber.*, **33**, 980 (1900).

(2) S. Gabriel and J. Colman, *Ber.*, **33**, 2630 (1900).

(3) G. W. Ewing and E. A. Steck, *J. Am. Chem. Soc.*, **68**, 2181 (1946).

(4) A. Albert and J. N. Phillips, *J. Chem. Soc.*, 1294 (1956).