min. at 25°, the mixture was concentrated under reduced pressure to one-third its volume and was diluted with 30 g. of ice. The precipitate was collected by filtration, washed with water, and dried to give 386 mg. Recrystallization from chloroform-ether gave 318 mg. (91%); m.p. 262–275°. After decolorization with Norite in chloroform-methanol, followed by several recrystallizations from chloroform-ether, the analytical sample melted at 267–282°; $[\alpha]_D$ −154° (chloroform); infrared spectrum: 6.05, 6.25 μ (pyridone).

Anal. Calcd. for $C_{24}H_{29}NO$ (347.48): C, 82.95; H, 8.41; N, 4.04. Found: C, 82.70; H, 8.26; N, 3.94.

B. A solution of 35 mg. (0.0001 mole) of 14-anhydroscillaridin A,[7] 100 mg. (0.0013 mole) of ammonium acetate and 0.01 ml. (0.00016 mole) of glacial acetic acid in 3 ml. of dimethylformamide was sealed in a Pyrex tube and heated at 150° for 3 hr. After the solution had been diluted with 6 ml. of water, the amorphous precipitate was collected by filtration, washed with water, and dried to give 23 mg. Recrystallization from methanol-ether, after decolorization with Norite, gave 4 mg. of crystalline material; m.p. 260–275°; mixed melting point with the product prepared according to procedure A, 260–275°; infrared spectrum: identical with that of the product prepared according to procedure A.

*3β,14β-Dihydroxy-17ξ-(2′-hydroxy-5′-pyridyl)-4-androstene 3β-*D*-gluco-*L*-rhamnoside (pyridone counterpart of scillaren A)* (IV). A solution of 346 mg. (0.0005 mole) of scillaren A, 650 mg. (0.0084 mole) of ammonium acetate, and 0.1 ml. (0.0016 mole) of glacial acetic acid in 8 ml. of dimethylformamide, together with a magnetic bar, was sealed under nitrogen in a Pyrex tube and heated with stirring for 4 hr. at 180°. The solution was concentrated nearly to dryness under diminished pressure to give a residue which was washed with 5 ml. of ether and with 10 ml. of acetone. A solution of the solid in 40 ml. of chloroform-ethanol (2:1) was washed with water and was dried over anhydrous sodium sulfate. The filtrate from the desiccant was concentrated under reduced pressure to give 320 mg. of amorphous residue. Recrystallization from methanol-acetone gave 125 mg. (36%); m.p. 250–267°. Several recrystallizations from methanol-acetone afforded fine rosettes of needles; the analytical sample was dried 4 hr. at 100° and 0.02 mm.; m.p. 283–284°; infrared spectrum: 6.05, 6.25 μ (pyridone).

Anal. Calcd. for $C_{36}H_{53}NO_{12}$ (691.83): C, 62.53; H, 7.72; N, 2.03. Found: C, 62.74; H, 7.88; N, 2.10.

A solution of 230 mg. (0.0003 mole) of IV and 3 ml. of acetic anhydride in 3 ml. of anhydrous pyridine was kept at 0° for 72 hr. The mixture was concentrated under reduced pressure to give a residue which was dissolved in chloroform. The solution was washed with 2*N* aqueous hydrochloric acid, with 2*N* aqueous sodium carbonate, and with water and was dried over anhydrous sodium sulfate. The filtrate from the desiccant was concentrated under reduced pressure. Recrystallization of the residue (323 mg.) from methanol-ether gave 233 mg., m.p. 170–175°. A chloroform solution of this material was filtered through silica gel. The residue from vacuum evaporation of the solvent was recrystallized from methanol to afford 127 mg. (45%) of very fine needles of the hexaacetyl derivative of IV; m.p. 239–242°/270–280°; infrared spectrum: 5.80 (acetoxy), 6.05, 6.25 μ (pyridone).

*3β,14β,-Dihydroxy-17ξ-(2′-hydroxy-5′-pyridyl)-4-androstene 3β-*L*-rhamnoside (pyridone counterpart of proscillaridin* A). A solution of 106 mg. (0.0002 mole) of proscillaridin A, 300 mg. (0.004 mole) of ammonium acetate and 0.1 ml. (0.0016 mole) of glacial acetic acid in 1 ml. of dimethylformamide was sealed in a Pyrex tube and heated for 3 hr. at 160°. The mixture was concentrated under reduced pressure to give a residue which was washed with ether and with acetone. A solution of the solid in chloroform-ethanol (2:1) was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. Recrystallization of the residue from methanol-ether gave 46 mg. (43%) of brown crystalline material; m.p. 283–286°. A methanolic solution of this product was decolorized with Norite. Two recrystallizations from methanol-acetone gave 19 mg. of triangular plates with convex sides; m.p. 289–292°; infrared spectrum: 6.05, 6.25 μ (pyridone).

Anal. Calcd. for $C_{30}H_{43}NO_7$ (529.65): N, 2.64. Found: N, 2.61.

N-Nitrosolactam of hydrogenation product of 17ξ-(2′-hydroxy-5′-pyridyl)-3,5,14-androstatriene. A solution of 315 mg. (0.001 mole) of 17ξ-(2′-hydroxy-5′-pyridyl)-3,5,14-androstatriene (III) and 1 drop of concd. hydrochloric acid in 70 ml. of glacial acetic acid was shaken with hydrogen in the presence of 60 mg. of platinum oxide for 15 hr. at 26°. A total of 140.6 ml. of hydrogen was taken up (theory for five double bonds plus catalyst: 125 ml.). After the catalyst had been removed by filtration, the solution was concentrated under diminished pressure to give a residue which was diluted with chloroform. The chloroform solution was washed with 2*N* aqueous sodium carbonate and with water and was dried over anhydrous sodium sulfate. Vacuum concentration of the filtrate from the desiccant gave 360 mg. of amorphous material which was crystallized from chloroform-ether to afford 269 mg. (82%) of crystalline product; m.p. 200–260°.

To a solution of 218 mg. (0.00067 mole) of this material and 0.8 ml. of glacial acetic acid in 5 ml. of acetic anhydride at 10–15° was added (in small portions during 4 hr.) 800 mg. of sodium nitrite.[8] After addition of 25 ml. of ice water, the mixture was extracted with ether. The organic phase was washed with water and was dried over anhydrous sodium sulfate. Concentration of the filtrate from the desiccant gave a residue which was crystallized from ether-petroleum ether (b.p. 30–60°) to afford 61 mg. (25%) of yellow crystalline product; m.p. 160–170°; infrared spectrum: 5.80 μ.[9]

Acknowledgment. The authors are greatly indebted to Dr. J. Renz, Sandoz AG, Basel, for gifts of scillaridin A, proscillaridin A, and scillaren A, and for pharmacological results; to Professor T. Reichstein, University of Basel, for provocative comments; and to the National Heart Institute of the National Institutes of Health, United States Public Health Service (H-2205) and the Eugene Higgins Trust for financial support.

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Preparation of Trimethylsilyl-Substituted Dihydric Phenols and Trimethylsilylbenzoquinone

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Received April 28, 1961

It was recently shown that trimethylsilyl-substituted aryloxytrimethylsilanes can be converted to the corresponding phenols without loss of trimethylsilyl groups from the ring by dissolving the

TABLE I

ARYLOXYTRIMETHYLSILANES

Compound	Yield, %	B.P. Mm.		n_D^{20}	C, % Calcd.	C, % Found	N, % Calcd.	N, % Found	Si, % Calcd.	Si, % Found
2,5-$[(CH_3)_3SiO]_2C_6H_3Cl$	82	81	0.2	1.4822	49.9	49.9	7.3	7.7	19.4	18.7
2,4-$[(CH_3)_3SiO]_2C_6H_3Cl$[a]	97	88	0.2	1.4827	—	—	—	—	—	—
3,4-$[(CH_3)_3SiO]_2C_6H_3Cl$	61	92	0.3	1.4820	49.9	50.1	7.3	7.9	19.4	19.6
2,5-$[(CH_3)_3SiO]_2C_6H_3SiCH_3$	73	93	0.4	1.4761	55.2	55.6	9.3	9.3	25.8	26.0
2,4-$[(CH_3)_3SiO]_2C_6H_3SiCH_3$[b]	85	155	14.0	1.4790	—	—	—	—	—	—
3,4-$[(CH_3)_3SiO]_2C_6H_3SiCH_3$	72	93	13.0	1.4720	55.2	55.3	9.3	9.0	25.8	26.3

[a] Lit. (ref. 2), b.p. 153°/25 mm.; n_D^{25} 1.4818. [b] Lit. (ref. 2) b.p. 169°/19 mm.; n_D^{25} 1.4772.

aryloxysilane in a concentrated solution of sodium methoxide in methanol, diluting with water, and extracting the phenol with pentane.[1] This method was used to prepare a number of poly(trimethylsilyl)phenols which could not be obtained by the usual methods of hydrolysis because of aryl-silicon cleavage.

No dihydric phenols having trimethylsilyl substituents on the ring have been reported. Attempts to obtain 4-(trimethylsilyl)resorcinol by hydrolysis of 2,4-bis(trimethylsiloxy)-trimethylsilylbenzene were unsuccessful because of desilylation during hydrolysis.[2] We therefore decided to apply the sodium methoxide procedure to the preparation of this compound and other trimethylsilyl-substituted dihydric phenols.

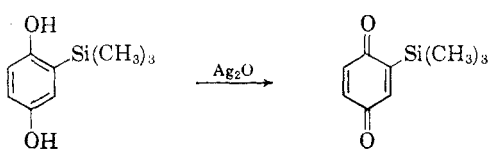
Chlorohydroquinone, 4-chlororesorcinol, and 4-chlorocatechol were converted to the corresponding trimethylsilyl ethers and the ring chlorine was then replaced by a trimethylsilyl group following procedures previously described.[1-3] The properties of the aryloxysilanes are listed in Table I.

Conversion of the trimethylsilyl ethers to the corresponding trimethylsilyl-substituted phenols by reaction with sodium methoxide solution was carried out successfully in the case of the hydroquinone and catechol derivatives. A 68% yield of trimethylsilylhydroquinone was obtained by allowing 2,5-bis(trimethylsiloxy)trimethylsilylbenzene to react for one hour with 4.5*M* sodium methoxide solution, diluting with water, and neutralizing with acetic acid. The yield of 4-trimethylsilylcatechol from 3,4-bis(trimethylsiloxy)trimethylsilylbenzene was lower and this product was usually contaminated with some catechol. The best results were obtained by using a concentrated (4.5*M*) sodium methoxide solution and the shortest reaction time which was compatible with complete hydrolysis of the silyl ether.

Several attempts to prepare 4-(trimethylsilyl) resorcinol in this fashion were unsuccessful. Aryl-silicon cleavage occurred in each case, so that the only product isolated was resorcinol, as in the aqueous hydrolysis previously reported by Speier.[2]

The failure of the reaction with the resorcinol derivative is not surprising. Aromatic desilylation reactions have, in general, the characteristics of electrophilic aromatic substitution, being accelerated by electron-donating groups and retarded by electron-withdrawing groups.[4] In the resorcinol derivative the carbon atom with the silicon substituent is very strongly activated, having a hydroxy group both *ortho* and *para*. The hydroquinone and catechol compounds have only one *ortho* or *para* hydroxy substituent. The other hydroxyl group is in the *meta* position and would be expected, by its electron-withdrawing inductive effect, to stabilize the phenol towards desilylation.[5]

Oxidation of trimethylsilylhydroquinone with silver oxide yielded bright yellow needles of trimethylsilylbenzoquinone-1,4, which is believed to be first reported example of a silicon-substituted quinone.



EXPERIMENTAL

Materials. Chlorohydroquinone, 4-chlororesorcinol, 4-chlorocatechol, and trimethylchlorosilane were commercially available materials which were used without further purification.

Trimethylsilyl ethers. The chlorophenols were converted to trimethylsilyl ethers by refluxing in toluene with trimethylchlorosilane and pyridine and were purified by fractional distillation under reduced pressure. Reaction of the trimethylsilyl ethers with sodium and trimethylchlorosilane in refluxing toluene yielded the trimethylsilyl-substituted aryloxytrimethylsilanes, which were also purified by vacuum distillation.

(Trimethylsilyl)hydroquinone. A small flask containing 3.26 g. (0.01 mole) of 2,5-bis(trimethylsiloxy)trimethylsilylbenzene was swept out thoroughly with nitrogen and

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(5) It is not known at what stage of the reaction desilylation takes place. It may involve either phenol, phenoxide ion, or, less probably, the trimethylsilyl ether. It seems likely that it occurs by reaction of the phenoxide ion with either methanol or water (after dilution) as the electrophilic agent. The observed order of reactivity would be expected in any case.

6.5 ml. of a 4.5*M* 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 2*M* 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 4.5*M* 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 2*M* 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 2*M* sodium methoxide or 15 min. with a 4.5*M* 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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Derivatives of 1-Thia-4,5-diazacyclohepta-2,4,6-triene. IV.[1] Systems Containing Chloro Substituents

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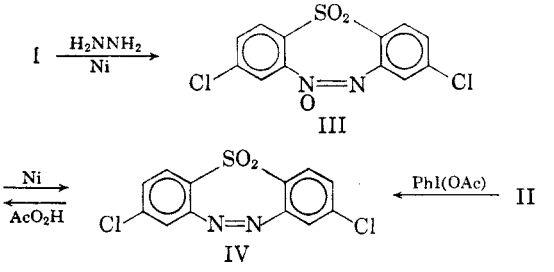
Received April 26, 1961

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

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

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