

## The Synthesis, Stability, and Sulfur-Elimination Reactions of Some Bis(N-arylimidoyl) Disulfides

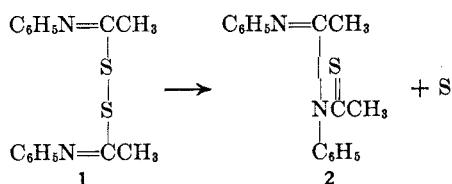
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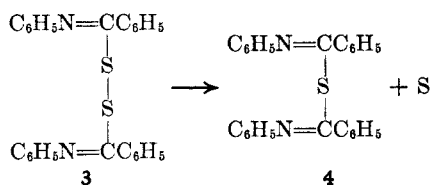
A new and general method for the synthesis of bis(N-arylimidoyl) disulfides by oxidation of the corresponding N-arylthioamides with iodine is described. Stability studies carried out on the bis(N-arylimidoyl) disulfides show that electron-withdrawing groups in the *para* position of the benzene ring of bis(N-phenylacetimidoyl) disulfide enhance the stability of the disulfide, whereas electron-supplying groups decrease the stability of the disulfide. Structural variation in the N-arylimidoyl functional group of bis(N-phenylacetimidoyl) disulfide markedly affects the course of its chemical reactions.

Bis(N-phenylacetimidoyl) disulfide (1) and N-(N'-phenylacetimidoyl)thioacetanilide (2) are found in cultures of a *Comamonas* sp. grown in 24 hr on a thioacetanilide medium.<sup>1</sup> Formation of 2 in the cultures is probably due to the elimination of a sulfur atom from 1.



Any attempt to understand the metabolic processes that occur when thioacetanilide is attacked by this organism would be facilitated by knowledge of the synthesis and sulfur elimination reactions of bis(N-arylimidoyl) disulfides.

Very few published reports on the synthesis and chemical reactions of this disulfide system are available. Hodosan and Serban<sup>2</sup> reported that bis(N-phenylbenzimidoyl) disulfide (3) is produced when a mixture of thiobenzanilide and benzoyl peroxide is heated to 51°. At 110°, bis(N-phenylbenzimidoyl) sulfide (4) is produced. Sulfide 4 may also be pro-



duced by heating 3 in the presence of benzoyl peroxide at 110°. Heyns and Bebenburg<sup>3</sup> prepared 4 by treatment of thiobenzanilide with nitrosyl chloride. Bis-(N-*p*-nitrophenylbenzimidoyl) disulfide was synthesized by Rivier and Zeltner<sup>4a</sup> by treatment of *p*-nitrothiobenzanilide with alkaline potassium ferriyanide; thiobenzanilide and several other N-*p*-phenyl-substituted thiobenzanilides yielded benzothiazoles.<sup>4b</sup>

This paper describes a new and general method for the synthesis of bis(N-arylimidoyl) disulfides by oxidation of the corresponding N-arylthioamides with iodine and demonstrates that structural variation in the N-arylimidoyl functional group of the disulfide

markedly affects its stability and the course of its chemical reactions.

Bis(N-arylimidoyl) disulfides were obtained in yields ranging from 7.5 to 78% by treatment of the corresponding N-arylthioamides with iodine in the presence of pyridine or tributylamine. In the absence of a base, tars were produced and only a trace of disulfide was detected by thin layer chromatography. In order to obtain satisfactory yields of several of the disulfides (Table I), it was necessary to replace ether as the solvent with an ether-dioxane mixture, thereby obtaining better solubilization of the N-arylthioamide.

The molecular weights obtained on the N-arylthioamide oxidation products (Table I) show that the compounds are composed of two molecules of the corresponding N-arylthioamide.

The nmr spectrum of bis(N-phenylacetimidoyl) disulfide contains a singlet at  $\delta = 2.40$  ppm (three methyl protons; width at half-band height, 0.21 ppm) and bands around  $\delta = 7.10$  ppm (five aromatic protons); bis(N-*p*-nitrophenylacetimidoyl) disulfide contains a singlet at  $\delta = 2.40$  ppm (three methyl protons; width half-band height, 0.01 ppm) and bands around  $\delta = 7.60$  ppm (four aromatic protons characteristic of a *para*-substituted benzene); bis(N-*p*-chlorophenylacetimidoyl) disulfide contains a singlet at  $\delta = 2.35$  ppm (three methyl protons; width at half-band height, 0.20 ppm) and bands around  $\delta = 7.00$  ppm (four aromatic protons characteristic of *para*-substituted benzene); bis(N-*p*-methylphenylacetimidoyl) disulfide contains bands at  $\delta = 2.34$  and 2.50 ppm (six methyl protons) and bands around  $\delta = 6.95$  ppm (four aromatic protons characteristic of *para*-substituted benzene); bis(N-1-naphthylacetimidoyl) disulfide contains a singlet at  $\delta = 2.40$  ppm (three methyl protons; width at half-band height, 0.28 ppm) and bands around  $\delta = 7.25$  ppm (seven aromatic protons); and bis(N-phenylbenzimidoyl) disulfide contains bands around  $\delta = 7.00$  ppm (ten aromatic protons).

The nmr spectrum for each of the N-arylthioamide iodine oxidation products is consistent with a disulfide structure. The band width at half-band height is reported for the methyl groups [N=C(CH<sub>3</sub>)S] in the bis(N-arylacetimidoyl) disulfides because this band is broader than expected. The broadness of the methyl absorptions is possibly due to the quadruple relaxation effect of the nitrogen atoms. This band broadness is also observed for bis(N-*p*-methylphenylacetimidoyl) disulfide. However, no value for the band width at half-band height was reported because the band is complicated by aromatic methyl absorption. Inter-

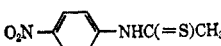
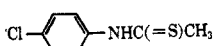
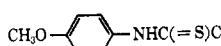
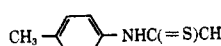
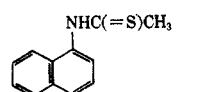
(1) C. T. Goodhue, J. R. Schaeffer, H. A. Risley, and R. V. VanSickle, unpublished work.

(2) F. Hodosan and N. Serban, *Bull. Soc. Chim. France*, 507 (1959).

(3) K. Heyns and W. V. Bebenburg, *Chem. Ber.*, **89**, 1303 (1956).

(4) (a) H. Rivier and J. Zeltner, *Helv. Chim. Acta*, **20**, 691 (1937); (b) R. N. Hurd and G. DeLa Mater, *Chem. Rev.*, **61**, 45 (1961).

TABLE I  
 DISULFIDES PRODUCED BY THE OXIDATION OF THIOAMIDES

Disulfide of	Base	Solvent	Yield, %	Mp, °C	Mol wt <sup>a</sup>		Anal., %							
					Calcd	Found	C		H		N		S	
$C_6H_5NHC(=S)CH_3$	$(C_4H_9)_3N$	Ether	72.9	48.5-50.5	300.5	312	64.0	63.9	5.4	5.4	9.3	9.3	21.3	21.0
	$(C_4H_9)_3N$	Ether-dioxane	53.2	142-144	390	404	49.2	49.3	3.6	3.5	14.4	14.1	16.4	16.5
	$(C_4H_9)_3N$	Ether-dioxane	78	105-106	369	368	52.0	51.8	3.5	3.8	7.5	7.2	17.3	17.1
	$(C_4H_9)_3N$	Ether	7.5	Oil	360.5 <sup>b</sup>	...	59.9	60.1	5.6	5.9	7.8	7.5	...	...
	$(C_4H_9)_3N$	Ether-dioxane	46	76-77	328	325	65.8	66.0	6.1	6.1	8.5	8.4	19.5	19.6
	$C_6H_5N$	Ether	35.9	46-47	400.5	405	71.9	72.1	5.0	5.1	6.9	6.8	16.0	16.0
$C_6H_5NHC(=S)C_6H_5$	$(C_4H_9)_3N$	Ether-dioxane	75	102-104	425	422	73.6	73.5	4.8	4.8	6.6	6.3	15.1	14.8

<sup>a</sup> Molecular weight determinations were carried out by the ebullioscopic method, with benzene as the solvent. <sup>b</sup> Bis(N-*p*-methoxyphenylacetimidoyl) disulfide was found to be too unstable for a molecular weight determination.

estingly enough, the sharpness of the methyl band for bis(N-*p*-nitrophenylacetimidoyl) disulfide may be due to a *p*-nitro group modification of the electron distribution around the nitrogen atom that reduces the quadruple broadening observed in the other bis(N-arylacetimidoyl) disulfides.

Infrared spectra (Table II) show the presence of phenyl and >NH groups in the N-arylthioamide and the >C=N group and the absence of the >NH group in the corresponding iodine oxidation product.

 TABLE II  
 INFRARED ABSORPTION OF N-ARYLTHIOAMIDES AND THE  
 CORRESPONDING IODINE OXIDATION PRODUCTS

Compd	N-Arylthioamide absorption, $\mu^a$		Oxidation product absorption, $\mu^c$	
	Ar	NH	C=N	NH
Thioacetanilide	6.25, 6.68	2.98, 6.50	6.09	None
<i>p</i> -Nitrothioacetanilide	6.21, 6.28, 6.62	2.98, 6.50	6.04	None
<i>p</i> -Chlorothioacetanilide	6.32, 6.75	2.98, 6.56	6.11	None
<i>p</i> -Thioacetaniside	6.30	2.98, 6.55	6.13 <sup>b</sup>	None
<i>p</i> -Thioacetotoluidide	6.29, 6.63	2.98, 6.55	6.11	None
N-1-Naphthylthioacetamide	6.28, 6.65	2.99	6.13	None
Thiobenzanilide	6.30, 6.71	2.98, 6.56	6.23, 6.32 <sup>c</sup>	None

<sup>a</sup> The absorption at 2.99  $\mu$  was observed on using a CS<sub>2</sub> solution of each compound. The absorption in the regions 6.1, 6.3, and 6.5  $\mu$  was observed with KBr pressings of the compounds. <sup>b</sup> The absorption of bis(N-*p*-methoxyphenylacetimidoyl) disulfide was observed with a film on a sodium chloride crystal. <sup>c</sup> The doublet observed for bis(N-phenylbenzimidoyl) disulfide may be due either to splitting of the phenyl band or to the group C<sub>6</sub>H<sub>5</sub>N=C<sub>6</sub>H<sub>5</sub>.

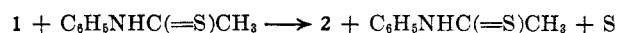
A disulfide structure appears to be the only structure for the iodine oxidation products that is consistent with the molecular weight, nmr, and infrared data.

During the course of synthesis of the bis(N-aryl-imidoyl) disulfides, differences in the stability of each of the disulfides were noted. Decomposition of the bis(N-arylimidoyl) disulfides probably is due to susceptibility of the disulfides to autoxidation. Prod-

ucts of decomposition were separated by thin layer chromatography, but these products were not identified in this study. The most stable disulfide exhibited no decomposition after exposure to air for 5 days at 25°, while the least stable disulfide began to decompose within 2 hr after isolation and purification. The disulfides may be arranged in the following decreasing order of stability: bis(N-phenylbenzimidoyl) disulfide (3), bis(N-*p*-nitrophenylacetimidoyl) disulfide, and bis(N-*p*-chlorophenylacetimidoyl) disulfide are more stable than bis(N-phenylacetimidoyl) disulfide (1), bis(N-*p*-methylphenylacetimidoyl) disulfide, and bis(N-1-naphthylacetimidoyl) disulfide; bis(N-*p*-methoxyphenylacetimidoyl) disulfide is the least stable in the series. Electron-withdrawing substituents in the *para* position of the benzene ring enhance the stability of the disulfide, whereas electron-supplying substituents decrease the stability of the disulfide. An increase in the electron-donating character of the *para* substituents of aromatic disulfides leads to a more facile splitting of the S-S bond by a free-radical mechanism.<sup>5</sup> A similar order of stability is observed for the bis(N-arylacetimidoyl) disulfides which possess structural similarity to the aromatic disulfides discussed in Schmidt's paper. Therefore decomposition of the bis(N-arylimidoyl) disulfides when exposed to air may involve homolysis of the S-S bond, although we obtained no direct evidence for this.

In refluxing ligroin (95°), 3 is converted to 4 in 76% yield. All of the bis(N-arylacetimidoyl) disulfides decompose to tars under these conditions.<sup>6</sup> Analysis of the tars by infrared spectroscopy did not show the presence of disulfide.

Treatment of compound 1 with thioacetanilide in acetone, at 30° for 5 days, produced 2 in 4% yield. A

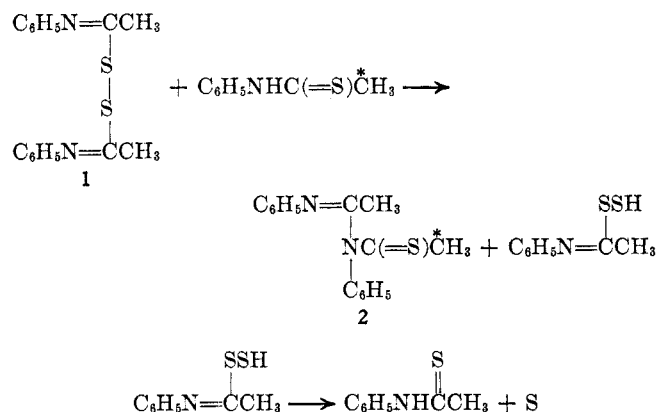


control containing only 1 was found to contain trace amounts of 2 and thioacetanilide after 5 days and was completely decomposed to a complex mixture of prod-

(5) U. Schmidt and A. Miller, *Ann. Chem.*, **672**, 91 (1964).

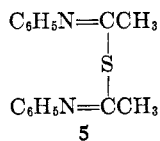
(6) Tar formation also occurs when the bis(N-arylacetimidoyl) disulfides are heated in refluxing ligroin under nitrogen.

ucts after 21 days. Since **1** decomposes more rapidly in acetone when thioacetanilide is present, it appears that thioacetanilide is involved in the decomposition of the disulfide. The instability of **1** at 30° produces the initial quantity of thioacetanilide observed in the control after 5 days. The following describes a probable course of the sulfur-elimination reaction.



Similar reactions were assumed to have occurred when the *para*-substituted bis(*N*-phenylacetimidoyl) disulfides and bis(*N*-1-naphthylacetimidoyl) disulfide were treated with the corresponding *N*-arylthioamide. Mixtures of products were separated by thin layer chromatography, but, since the corresponding thioacylated acetamidines were not available, the reactions were not investigated in detail.

A slightly different course of reaction was observed when disulfide **3** was treated with thiobenzanilide at 30° for 5 days. Sulfide **4** was produced in 28.8% yield. A control experiment did not exhibit any decomposition over a 5-day period. Similarly, sulfide **4** was also produced in 28.5% yield when **3** was treated with sodium iodide in acetone at 30°. Treatment of **1** with sodium iodide in acetone at 30° produced a mixture of products, which were observed by thin layer chromatography. One of the components of this mixture was an  $R_f$  value identical with the  $R_f$  value of an unstable metabolite produced in cultures of the *Comamonas* sp.<sup>1</sup> By analogy with the reaction of sodium iodide with **3**, this compound may be expected to be bis(*N*-phenylacetimidoyl) disulfide (**5**).



During the course of the investigation of the effects of heat, sodium iodide, and the corresponding *N*-arylthioamide on structural variations of disulfide **1**, it became apparent that the structure of the disulfide exerted an effect on the course of its sulfur-elimination reaction. Disulfide **1** produced **2** and several unstable substances when treated with thioacetanilide, whereas disulfide **3** produced a stable product (**4**) when treated with thiobenzanilide.

Attempts to obtain **2** by a sulfur-elimination reaction were successful in only one of the reactions studied, treatment of **1** with thioacetanilide. Since an excess of thioacetanilide is present in cultures of the *Coma-*

*monas* sp., some or all of compound **2** present in the cultures may be due to the interaction of thioacetanilide with **1**.

### Experimental Section<sup>7</sup>

**Starting Materials.**—Silica gel G was obtained from Brinkman Instruments (Westbury, N. Y.). Woelm neutral alumina was obtained from Alupharm Chemical Co. (New Orleans, La.). Thioacetanilide, thiobenzanilide, *p*-nitrothioacetanilide, *N*-1-naphthylthioacetamide, *p*-chlorothioacetanilide, *p*-thioacetanilide, *p*-thioacetotoluidide, tributylamine, pyridine, iodine, and sodium iodide were obtained from Eastman Kodak Co.

**Thin Layer Chromatographic Analysis.**—Thin layer chromatographic analyses of the reaction mixtures, of the purified bis(*N*-arylthioamide) disulfides, and of the stability test reaction mixtures were carried out on silica gel G plates (0.25 mm) with a hexane-acetone solvent system (7:2, v/v), with *N*-2,6-trichloroquinoneimine as the indicator.<sup>8</sup>

**Bis(*N*-phenylacetimidoyl) Disulfide (**1**).**<sup>9</sup>—In 150 ml of anhydrous ether 8.0 g (0.052 mole) of thioacetanilide and 11.0 g (0.06 mole) of tributylamine were dissolved. To the stirred solution, cooled to 0–5°, 6.6 g (0.026 mole) of iodine dissolved in 150 ml of anhydrous ether was added dropwise over a period of 0.75 hr. Upon completion of the iodine addition, the reaction mixture was stirred for 2 hr at 5°. Solid tributylamine hydroiodide was removed by using suction filtration and washed with a minimum amount of anhydrous ether. The combined wash and filtrate were evaporated at room temperature under water-aspirator vacuum. The dark yellow liquid residue was dissolved in 15 ml of anhydrous ether and chromatographed on a 3.8 × 85 cm column containing 500 g of Woelm neutral alumina, activity grade III. The column was eluted with a total of 3 l. of a hexane-acetone mixture. The acetone concentration was progressively varied from 0 to 10%. Fractions were collected with a fraction collector.

The tubes which contained **1** were determined by thin layer chromatography. The  $R_f$  value is 0.51 for **1** and 0.26 for thioacetanilide. The tubes containing **1** were combined and the solvent was reduced to one-tenth of its original volume at room temperature (water-aspirator vacuum). On standing for several days in the refrigerator, the product crystallized. It was collected by suction filtration and washed with a minimum amount of hexane.<sup>10</sup> The product weighed 5.7 g. The yield of **1** was 72.9%.

**Solvent Modification.**—In the disulfide preparations in which ether was replaced with an ether-dioxane mixture (Table I), the iodine solutions were made up by dissolving iodine in ether. *p*-Thioacetotoluidide and thiobenzanilide were dissolved in dioxane. *p*-Chlorothioacetanilide was dissolved in a mixture of 1 part of dioxane and 2.5 parts of ether. *p*-Nitrothioacetanilide was dissolved in a mixture of 1.2 parts dioxane and 1 part of ether.

**Purification of Bis(*N*-arylthioamide) Disulfides.**—Disulfide **1** and bis(*N*-*p*-methoxyphenylacetimidoyl) disulfide were purified by column chromatography on Woelm neutral alumina, activity grade III. A gradient solvent system (0–10% acetone in hexane) was used. The acetone concentration was progressively varied from 0 to 10%. Bis(*N*-1-naphthylacetimidoyl) disulfide was purified by column chromatography on Woelm neutral alumina, activity grade III. A solvent mixture composed of hexane and acetone (9:1, v/v) was used. The remaining disulfides were purified by recrystallization. The crude disulfide was dissolved in a minimum amount of hot acetone. Water was added to the hot solution until the product began to oil out or precipitate. Enough hot acetone was added to bring the product into solution. The recrystallization mixture was allowed to

(7) (a) All melting points are uncorrected; (b) microanalyses were made by the Microanalytical Laboratory of the Eastman Kodak Research Laboratories; (c) infrared spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer; (d) the nmr spectrum was determined on a Varian A-60 spectrometer (tetramethylsilane was used as an internal standard and  $\text{CDCl}_3$  was used as the solvent).

(8) H. D. Gibbs, *J. Biol. Chem.*, **72**, 649 (1927).

(9) The synthesis of **1** was carried out in the dark under nitrogen.

(10) In several runs, the product oiled out and would not crystallize, even in the presence of seed crystals. A second column chromatography did not yield a crystalline product. Analytical data indicated that the oil and crystalline disulfide were identical.

stand at room temperature for 24 hr and then placed in the refrigerator for several hours.

**Stability Tests on Bis(N-arylimido) Disulfides.**—The disulfides and dilute benzene solutions of the disulfides were exposed to air at 25°. Decomposition was detected by visual observations (darkening of the crystalline disulfide or of a solution of the disulfide) and by thin layer chromatography of the benzene solution.

**Control Experiments.**—A control experiment was carried out for each sulfur-elimination reaction studied. Mention of the control is made only in those experiments where some chemical change in the control was observed by thin layer chromatography.

**Effect of Heat on 3.**—In 20 ml of refluxing ligroin (95°) 0.2 g (0.00047 mole) of **3** was dissolved. During the 24-hr reflux period, crystals deposited from the solution. After the reaction mixture had cooled to room temperature, the yellow crystals were collected by suction filtration, washed with 5 ml of ligroin, and air dried. The product weighed 0.14 g, mp 202–204°. A mixture melting point with an authentic sample of **4** was not depressed.<sup>2</sup> The yield of **4** was 76.0%.

*Anal.* Calcd for C<sub>26</sub>H<sub>30</sub>N<sub>2</sub>S: C, 79.6; H, 5.1; N, 7.1; S, 8.2; mol wt, 392. Found: C, 79.2; H, 5.0; N, 7.0; S, 8.3; mol wt, 401 (benzene).

**Effect of Heat on 1.**—In 20 ml of refluxing ligroin (95°) 0.2 g (0.0067 mole) of **1** was dissolved. During the 18-hr reflux period, a black, tar-like solid formed. On standing at room temperature, the tar solidified. The solid was collected by suction filtration. It weighed 0.1 g. Thioacetanilide (*R<sub>f</sub>* 0.26) was found to be present in the filtrate and in an ether extract of the solid by using thin layer chromatography. An infrared spectrum of the solid showed a band at 6.5 μ characteristic of the >NH group.

**Treatment of 3 with Thiobenzanilide.**—In 25 ml of acetone 0.42 g (0.001 mole) of **3** and 0.42 g (0.002 mole) of thiobenzanilide were dissolved. The solution was shaken at 30° for 48 hr. During this time, a yellow, crystalline solid formed in the reaction mixture. The product weighed 0.15 g, mp 203–205°. A mixture melting point with an authentic sample of **4** was not depressed. The yield of **4** was 38.8%.

**Treatment of 1 with Thioacetanilide.**—In 25 ml of acetone 3.0 g (0.01 mole) of **1** and 3.0 g (0.02 mole) of thioacetanilide were dissolved. The solution was placed under nitrogen and

shaken at 30° for 5 days. The solvent was evaporated at room temperature under water-aspirator vacuum. The oil residue was dissolved in 10 ml of ether and the ether solution was chromatographed on a 3.8 × 85 cm column containing 500 g of Woelm neutral alumina, activity grade III. The procedure used to isolate **2** was the same as that used for isolation of **1**. The orange oil weighed 0.11 g (4.1%). An infrared spectrum and *R<sub>f</sub>* value (0.45) obtained on the sample were identical with those of an authentic sample of **2**.<sup>1</sup>

A control experiment carried out under the above conditions was analyzed by thin layer chromatography after 5 and 21 days. A trace of **2** was observed after 5 days. After 21 days, no disulfide **1** was detected in the control. A complex mixture composed of approximately 10 spots was observed by thin layer chromatography. Several of the compounds were colored prior to spraying with the indicator.

**Treatment of 3 with Sodium Iodide.**—In 20 ml of acetone, 0.42 g (0.001 mole) of **3** and 0.59 g (0.0040 mole) of sodium iodide were dissolved. The solution was shaken at 30° for 5 days. The solid which crystallized was collected by suction filtration and was washed with 10 ml of acetone. The yellow, crystalline product weighed 0.11 g, mp 211°. A mixture melting point with an authentic sample of **4** was obtained, mp 209–211°. The yield of product was 28.1%.

**Treatment of 1 with Sodium Iodide.**—In 20 ml of acetone, 0.3 g (0.001 mole) of **1** and 0.59 g (0.004 mole) of sodium iodide were dissolved. The solution was shaken at 30° for 5 days. The clear, yellow solution turned orange during this time and was analyzed after 5 days by thin layer chromatography. Spots corresponding to thioacetanilide (*R<sub>f</sub>* 0.26), **1** (*R<sub>f</sub>* 0.51), and a substance designated as metabolite C (*R<sub>f</sub>* 0.62), isolated from cultures of the *Comamonas* sp.<sup>12</sup> grown on thioacetanilide, were observed.<sup>1</sup>

**Acknowledgment.**—Grateful acknowledgment is made to Dr. T. H. Regan, for interpretation of the nmr spectra, and to Mr. W. Blum, for interpretation of the infrared spectra.

(11) Melting points of 203 and 213° have been reported for **4**.<sup>2</sup>

(12) NOTE ADDED IN PROOF.—Since the paper was submitted, the organism *Comamonas* sp. has been reclassified as a *Pseudomonas* sp.

## The Synthesis and Properties of Seven-, Eight-, and Nine-Membered Silicon Ring Systems

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Synthetic routes have been devised which provide convenient entry for the first time into organofunctional seven-, eight-, and nine-membered silicon ring systems. The acyloin-type ring closure was employed successfully to prepare 1,1-dimethyl-5-hydroxysila-4-cycloheptanone and 1,1-dimethyl-6-hydroxysila-5-cyclononane. The former was reduced successfully to 1,1-dimethylsila-4-cycloheptanone. The synthesis of 1,1-dimethylsila-5-cyclooctanone was also achieved, but in low yield, by pyrolysis of the appropriate thorium salt. Nmr spectral data are reported for all the silacyclic compounds which have been synthesized.

Recently we were led to investigate the possible synthesis of cyclic organosilanes of medium ring size. A review of the literature disclosed that there existed no reported representative of this type of compound which contained a functional group on the carbon portion of the heterocycle. Indeed, our survey disclosed that the only silacyclic compounds extant with a ring size greater than six are four silacycloheptanes,<sup>1</sup> variously substituted on silicon, and obtainable only in poor yields from the reaction of 1,6-hexamethylene-dimagnesium bromide with the appropriate chlorosilane. In view of the paucity of data in this area, we

were desirous of designing synthetically useful routes to such silacyclic systems. A logical starting point seemed to be an investigation of those ring-closure methods which are known to give respectable yields of medium size rings in the carbocyclic series. The acyloin ring closure<sup>2</sup> seemed particularly attractive in this regard. First of all, the yields in such reactions are generally good, and, secondly, the nature of the ring closure is such that it would occur at positions other than at silicon. The latter feature would necessarily lead to the formation of functional groups on the carbon portion of the heterocycle.

(1) R. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954); see also J. M. Hersh, U. S. Patent 2,615,033 (1952); *Chem. Abstr.*, **47**, 9344 (1953).

(2) S. M. McElvain, *Org. Reactions*, **4**, 262 (1948).