

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.² The yield of **4** was 76.0%.

Anal. Calcd for C₂₆H₃₀N₂S: 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_f* 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_f* value (0.45) obtained on the sample were identical with those of an authentic sample of **2**.¹

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_f* 0.26), **1** (*R_f* 0.51), and a substance designated as metabolite C (*R_f* 0.62), isolated from cultures of the *Comamonas* sp.¹² grown on thioacetanilide, were observed.¹

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**.²

(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

ROBERT A. BENKESER AND ROBERT F. CUNICO

Department of Chemistry, Purdue University, West Lafayette, Indiana

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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,¹ 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 closure² 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).

TABLE I
NUCLEAR MAGNETIC RESONANCE SPECTRA OF VARIOUS SILANES^{a,b}

Silane	τ values
1. $(\text{CH}_3)_2\text{Si}(\overset{1}{\text{CH}_2}\overset{2}{\text{CH}_2}\overset{3}{\text{CO}}\overset{4}{\text{CH}_3})_2$	10.00 (H ¹ singlet), 9.18 (H ² multiplet), 7.75 (H ³ multiplet), 6.41 (H ⁴ singlet)
2. $(\text{CH}_3)_2\text{Si}(\overset{1}{\text{CH}_2}\overset{2}{\text{CH}_2}\overset{3}{\text{CHO}}\overset{4}{\text{H}}\overset{5}{\text{CO}}\overset{6}{\text{CH}_2}\overset{7}{\text{CH}_2})_2$	10.00 and 10.11 (H ¹ two singlets), 9.35 (H ² , H ⁷ multiplet), 8.01 (H ³ multiplet), 7.47 (H ⁶ multiplet), 5.91 (H ⁵ broad singlet), 5.81 (H ⁴ triplet)
3. $(\text{CH}_3)_2\text{Si}(\overset{1}{\text{CH}_2}\overset{2}{\text{CH}_2}\overset{3}{\text{CH}_2}\overset{4}{\text{CO}}\overset{5}{\text{CH}_2}\overset{6}{\text{CH}_2})_2$	9.91 (H ¹ singlet), 9.20 (H ² , H ⁶ multiplet), 8.10 (H ³ complex pattern), 7.54 (H ⁴ , H ⁵ multiplet)
4. $(\text{CH}_3)_2\text{Si}(\overset{1}{\text{OCH}_2}\overset{2}{\text{CH}_2}\overset{3}{\text{CH}_2}\overset{4}{\text{CH}_2}\overset{5}{\text{CH}_2}\text{Cl})_2$	9.92 (H ¹ singlet), 7.8–8.6 (H ³ , H ⁴ envelope), 6.38 (H ² , H ⁵ pair of merged triplets)
5. $(\text{CH}_3)_2\text{Si}(\overset{1}{\text{CH}_2}\overset{2}{\text{CH}_2}\overset{3}{\text{CH}_2}\overset{4}{\text{CH}_2}\overset{5}{\text{COH}})_2$	10.0 (H ¹ singlet), 9.45 (H ²), 8.5 (H ³ , H ⁴), 7.5 (H ⁵ hydrogen bonded), 6.38 (H ⁵), 5.15 (H ⁵ free). All absorptions but H ¹ are broad bands
6. $(\text{CH}_3)_2\text{Si}(\overset{1}{\text{CH}_2}\overset{2}{\text{CH}_2}\overset{3}{\text{CH}_2}\overset{4}{\text{CO}_2}\overset{5}{\text{H}})_2$	10.05 (H ¹ singlet), 9.52 (H ² multiplet), 8.41 (H ³ complex pattern), 7.71 (H ⁴ multiplet), -2.01 (H ⁵ singlet)
7. $(\text{CH}_3)_2\text{Si}(\overset{1}{\text{CH}_2}\overset{2}{\text{CH}_2}\overset{3}{\text{CH}_2}\overset{4}{\text{CO}_2}\overset{5}{\text{CH}_3})_2$	10.00 (H ¹ singlet), 9.53 (H ² multiplet), 8.41 (H ³ complex pattern), 7.73 (H ⁴ multiplet), 6.38 (H ⁵ singlet)
8. $(\text{CH}_3)_2\text{Si}(\overset{1}{\text{CH}_2}\overset{2}{\text{CH}_2}\overset{3}{\text{CH}_2}\overset{4}{\text{CHO}}\overset{5}{\text{H}}\overset{6}{\text{CO}}\overset{7}{\text{CH}_2}\overset{8}{\text{CH}_2}\overset{9}{\text{CH}_2})_2$	10.12 and 10.19 (H ¹ two singlets), 9.1–9.8 (H ² , H ⁹ complex pattern), 7.2–9.1 (H ³ , H ⁴ , H ⁷ , H ⁸ complex pattern), 5.84 (H ⁶ pair of merged doublets), 5.58 (H ⁵ broad singlet)
9. $(\text{CH}_3)_2\text{Si}(\overset{1}{\text{CH}_2}\overset{2}{\text{CH}_2}\overset{3}{\text{CH}_2}\overset{4}{\text{CHO}}\overset{5}{\text{H}}\overset{6}{\text{CH}_2}\overset{7}{\text{CH}_2}\overset{8}{\text{CH}_2}\overset{9}{\text{CH}_2}\overset{10}{\text{CH}_2})_2$	10.09 (H ¹ singlet), 9.37 (H ² , H ¹⁰ broad band), 8.42 (H ³ , H ⁴ , H ⁷ , H ⁸ , H ⁹ envelope), 7.94 (H ⁶ broad singlet), 6.30 (H ⁵ broad band)
10. $(\text{CH}_3)_2\text{Si}(\overset{1}{\text{CH}_2}\overset{2}{\text{CH}_2}\overset{3}{\text{CH}_2}\overset{4}{\text{CO}}\overset{5}{\text{CH}_2}\overset{6}{\text{CH}_2}\overset{7}{\text{CH}_2})_2$	10.06 (H ¹ singlet), 9.34 (H ² , H ⁷ multiplet), 8.11 (H ³ , H ⁶ complex pattern), 7.72 (H ⁴ , H ⁵ multiplet)

^a Unless otherwise stated, these spectra were determined in carbon tetrachloride solution with tetramethylsilane as an internal standard. A Varian A-60 nmr spectrometer was employed. Chemical shifts are in τ values and are measured to the estimated center on singlet or multiplet. Entries 2, 8, and 9 were determined in deuteriochloroform solution. Benzene was used as an internal standard in entries 2, 3, 6, 8, 9, and 10. ^b In the case of each of the spectra listed in this table, the peak areas were consistent with the proton assignments made.

oxidation of primary alcohols with chromic acid mixtures is a common occurrence and has received much attention mechanistically.⁹

Pyrolysis of the dry thorium salt of compound **13**, in a procedure patterned after the method of Ruzicka and co-workers,³ gave 1,1-dimethylsila-5-cyclooctanone (**15**) as the major component of the pyrolysate, but only in a 7% yield. In contrast, the one attempt made to form the nine-membered system by an acyloin ring closure of dimethyldi(3-carbomethoxypropyl)silane (**14**) gave cyclic material in about 50% yield. Two products were obtained in the latter case, however, 1,1-dimethyl-6-hydroxysila-5-cyclononane (**16**) and 1,1-dimethylsila-5-cyclononanol (**17**). It is possible that the latter material arose from a reduction of compound **16** by the excess sodium during the hydrolysis step. Since only small amounts of material were at hand, no attempt was made to substantiate this hypothesis.

In Table I are listed the nmr spectra of the compounds which have been synthesized and reported herein.

It is of interest, that the carbonyl absorption frequencies of the six- (5.87 μ),⁵ seven- (5.84 μ), and eight-membered (5.82 μ) silacyclic ketones are not appreciably different. The carbonyl stretching band of 1,1-diphenylsila-2-cyclohexanone occurs at 6.07 μ .¹⁰

(9) See W. A. Mosher and D. M. Preiss, *J. Am. Chem. Soc.*, **75**, 5605 (1953), and references cited therein.

(10) A. G. Brook and J. B. Pierce, *J. Org. Chem.*, **30**, 2566 (1965).

Experimental Section

Dimethyldi(3-chloropropoxy)silane (2).—This was prepared as described previously.⁴ Dimethyldichlorosilane, 258 g (2.0 moles), and 378 g (4.0 moles) of 3-chloro-1-propanol in 643 ml (8.0 moles) of pyridine gave 433 g (88%) of product boiling at 80–85° (1 mm), n_D^{20} 1.4413 [lit.⁴ bp 141° (25 mm), n_D^{20} 1.4413].

Dimethyldi(3-hydroxypropyl)silane (4).—A 5-l., three-neck flask was equipped with Trubore stirrer, addition funnel, and a 2-ft West condenser. Dry toluene (800 ml, filtered from calcium hydride) and 178 g (7.75 g-atoms) of sodium were added, the toluene was brought to reflux, and the mixture was stirred vigorously to form a sodium sand. There was then slowly added 105 g of trimethylchlorosilane followed by dropwise (overnight) addition of 433 g (1.77 moles) of dimethyldi(3-chloropropoxy)silane mixed with 316 g of trimethylchlorosilane (for a total of 421 g, 3.88 moles). The mixture was then cooled in an ice bath and hydrolysis was carried out by the addition of (1) 100 ml of ethanol, (2) 2000 ml of water, (3) 100 ml of concentrated hydrochloric acid in 400 ml of water, and (4) 500 ml of concentrated hydrochloric acid. The solution was allowed to stir overnight, the organic layer then was separated and combined with ethereal washings of the aqueous phase, and the liquid thus obtained was concentrated and distilled through a Todd column. After a forerun of 82.9 g of alcoholic material, bp 75–115° (0.4 mm), there was obtained 109 g (35%) of the desired diol, bp 115–120° (0.4 mm), n_D^{20} 1.4624 [lit.⁴ bp 176° (24 mm), n_D^{20} 1.4649].

Dimethyldi(2-carbomethoxyethyl)silane (6).—Oxidation of 109 g (0.620 mole) of dimethyldi(3-hydroxypropyl)silane with 236 g (1.66 moles) of potassium permanganate and 24 g (0.60 mole) of sodium hydroxide was carried out as reported⁶ to give dimethyldi(2-carboxyethyl)silane (**5**). The acid was not isolated, but esterified with diazomethane to yield 47.5 g (33%) of product boiling at 109–113° (2.3 mm). An analytically pure sample of the diester was obtained by preparative vpc (6-ft Ucon Polar, 150°), n_D^{20} 1.4435.

Anal. Calcd for $C_{10}H_{20}O_4Si$: C, 51.70; H, 8.68. Found: C, 51.83; H, 8.74.

1,1-Dimethyl-5-hydroxysila-4-cycloheptanone (7).¹¹—A 500-ml, three-neck Morton flask was equipped with Friedrichs condenser, drying tube, and addition funnel with attached nitrogen line. The system was flamed out under nitrogen flow. There was then added 90 ml of reagent grade toluene; the solvent was brought to reflux under nitrogen, and some vapor was allowed to escape to remove residual moisture. The toluene was stirred vigorously at reflux for 45 min to deoxygenate the liquid. After cooling, 14.0 g (0.609 g-atom) of sodium was added to the flask and the mixture was stirred with a high-speed stirrer while at reflux. Dimethyldi(2-carbomethoxyethyl)silane (7.0 g, 0.03 mole) in 30 ml of toluene was then added to the metal dispersion over 4 hr. Stirring was continued for 17.5 hr longer and hydrolysis was carried out by adding 14 ml of a 1:1 acetic acid-toluene mixture followed by 45 ml of water. After filtration, the organic layer was separated, then combined with benzene extracts of the aqueous phase, and dried (anhydrous magnesium sulfate). Distillation gave 1.8 g (28%) of product boiling at 60–64° (0.6 mm).

Anal. Calcd for $C_8H_{17}O_2Si$: C, 55.79; H, 9.37. Found: C, 56.04; H, 9.32.

A sample collected by vpc (12-ft Apiezon L, 192°) had refractive index n_D^{20} 1.4821. The semicarbazone melted at 160°.

Anal. Calcd for $C_9H_{19}N_3O_2Si$: C, 47.13; H, 8.35; N, 18.32. Found: C, 47.03; H, 8.36; N, 18.43.

1,1-Dimethylsila-4-cycloheptanone (8).—From 1.6 g (0.0093 mole) of the acyloin,⁹ treated first in benzene with 2 ml of propanedithiol, 3 g of zinc chloride, and dry hydrogen chloride, and then with 4 g of mercuric chloride and 6 g of cadmium carbonate in aqueous acetone, there was obtained 133 mg (9%) of vpc-collected (5-ft SE-30, 136°) ketone, n_D^{20} 1.4729. Its carbonyl absorption (neat liquid, Perkin-Elmer Model 421 spectrophotometer) was at 1702 cm^{-1} .

The 2,4-dinitrophenylhydrazone of this ketone melted at 94–95°.

Anal. Calcd for $C_{11}H_{20}N_4O_4Si$: C, 51.41; H, 6.33; N, 15.99. Found: C, 51.59; H, 6.30; N, 16.02.

Dimethyldi(4-chlorobutoxy)silane (10).⁸—An adaptation of a general method employed by Speier⁴ was used for the preparation of this compound. In a 1-l., three-neck flask equipped with stirrer, addition funnel, and condenser were placed 250 ml of carbon tetrachloride, 32.3 g (0.25 mole) of dimethyldichlorosilane, and 181 g (1.53 moles) of 4-chloro-1-butanol.⁷ After the chlorobutanol had been added to the reaction vessel, the addition funnel was replaced by a gas inlet tube extending below the surface of the liquid, and the mixture was stirred vigorously at reflux for 7 hr with nitrogen passing through the solution. At the end of this time, hydrogen chloride was still being evolved, and decomposition of excess starting alcohol was suspected. Accordingly, the solution was cooled to 30° and stirred overnight, resulting in a marked decrease in acid evolution, after which residual hydrogen chloride was removed by stirring the mixture under aspirator vacuum for 3 hr. Removal of the remaining solvent was accomplished using a rotary evaporator, and the residue was distilled through a Todd column. A forerun [bp up to 45° (0.5 mm)] yielded 95.5 g of 4-chloro-1-butanol, $n_D^{24.5}$ 1.4501 (lit.¹² n_D^{20} 1.4518), followed by about 20 g of a 3:1 mixture of 4,4'-dichlorodi-*n*-butyl ether and the desired product boiling at 50–105° (1.5 mm). There was then obtained 47.8 g (40%) of essentially pure dimethyldi(4-chlorobutoxy)silane boiling at 105–112° (1.5 mm). This compound appeared to be slightly unstable to vpc (5-ft Carbowax 20M TPA, 202°), and a sample stored at 30° for several months underwent decomposition to a two-phase mixture.

An analytical sample of dimethyldi(4-chlorobutoxy)silane was obtained by redistillation of the above material, bp 99° (0.10 mm), $n_D^{26.5}$ 1.4460.

Anal. Calcd for $C_{10}H_{20}Cl_2O_2Si$: C, 43.95; H, 8.12; Cl, 25.95. Found: C, 43.79; H, 8.31; Cl, 25.71.

Trimethyl(4-chlorobutoxy)silane (11).—This was synthesized from 94.0 g (0.87 mole) of tetramethylene chlorohydrin and 100 g (0.92 mole) of trimethylchlorosilane in benzene, using ammonia as the acid scavenger, essentially as reported.⁴ There was obtained 95.7 g (61.4%) of product boiling at 80–84°

(24 mm), n_D^{21} 1.4200 [lit.⁴ bp 81° (24 mm), n_D^{25} 1.4218]. Analysis by vpc (12-ft DEGS, 140°) indicated its purity to be in excess of 99%.

Dimethyldi(4-hydroxybutyl)silane (12). **A. From Rearrangement of Dimethyldi(4-chlorobutoxy)silane.**—This preparation was carried out essentially in the same manner as that for dimethyldi(3-hydroxypropyl)silane (4). There was employed 18 g (0.78 g-atom) of sodium, 43.1 g (0.158 mole) of dimethyldi(4-chlorobutoxy)silane, and 43 g (0.33 mole) of trimethylchlorosilane. After the usual work-up, 8.3 g of a murky liquid boiling at 120–146° (0.08 mm) was obtained. Spectral data, as well as elemental analyses, indicated the presence of siloxane contaminants in the product.

B. From Trimethyl(4-chlorobutoxy)silane (11).—A 1-l., three-neck flask fitted with a Friedrichs condenser, addition funnel, Trubore stirrer, and nitrogen inlet was charged with 15 g (0.62 g-atom) of magnesium turnings and then flamed out. About 500 ml of anhydrous ethyl ether was introduced together with several milliliters of methyl iodide. After reaction had been initiated, 95 g (0.53 mole) of trimethyl(4-chlorobutoxy)silane was added in one portion and the mixture was stirred for 12 hr. There was then added 34.2 g (0.26 mole) of dimethyldichlorosilane and stirring was continued for 12 hr at reflux, followed by 24 hr at room temperature. Water was added, insoluble matter was filtered off, and the organic layer was isolated and combined with ethereal extracts of the aqueous phase. Solvent was removed, and 300 ml of ethanol plus 150 ml of water was added to the residue; about 1 ml of concentrated hydrochloric acid was then introduced and the mixture was distilled until the majority of the solvent was removed. Vacuum distillation gave, after a small fore-run of trimethyl(4-hydroxybutyl)silane, 17.8 g (33%) of diol boiling at 119° (0.2 mm), n_D^{20} 1.4653.

Anal. Calcd for $C_{10}H_{24}O_2Si$: C, 58.80; H, 11.84. Found: C, 58.98; H, 11.83.

Dimethyldi(3-carbomethoxypropyl)silane (14).—A 200-ml flask was charged with 3.5 g (0.017 mole) of dimethyldi(4-hydroxybutyl)silane, 7.3 g (0.046 mole) of potassium permanganate, 0.5 g of sodium carbonate, and 150 ml of dry acetone. The mixture was refluxed for 26 hr and then poured into 200 ml of water; traces of permanganate were destroyed by adding sodium sulfite. Acetone removal was followed by ether extraction, leading to the recovery of 0.7 g of starting diol. The basic solution was then strongly acidified, and its ethereal extracts were treated with diazomethane. There was obtained 2 g (55% based on converted diol) of product boiling at 106–120° (0.5 mm) which vpc (6-ft Ucon Polar, 160°) indicated was about 90% pure. A vpc-collected sample possessed a refractive index $n_D^{29.7}$ 1.4436.

Anal. Calcd for $C_{12}H_{24}O_4Si$: C, 55.35; H, 9.29. Found: C, 55.51; H, 9.21.

Oxidation of the diol using chromium trioxide in 65% acetic acid-water, either in stoichiometric amounts or in excess, and using either normal or inverse addition, gave rise to low yields of diacid because a major side product was produced.

This material (after treatment with diazomethane) could not be distilled at 230° (0.45 mm) but was collected by vpc (2-ft silicone rubber, 245°), n_D^{30} 1.4580. Except for the presence of a 2-H triplet at τ 5.97, its nmr and infrared spectra were very similar to those of 1,1-dimethyldi(3-carbomethoxypropyl)silane.

Anal. Calcd for $C_{22}H_{44}O_6Si_2$: C, 57.35; H, 9.63. Found: C, 57.06; H, 9.49.

Dimethyldi(3-carboxypropyl)silane (13)—This diacid could not be induced to crystallize from the crude material obtained in the oxidation step; so pure samples were obtained by saponification of purified dimethyldi(3-carbomethoxypropyl)silane. In a typical run, 5.5 g (0.024 mole) of the diester was added to a solution of 5.5 g (0.14 mole) of sodium hydroxide in 50 ml of 1:1 ethanol-water and stirred at room temperature for 21 hr. Work-up gave 4.2 g (86%) of diacid (mp 40.0–43.0°) from ether-hexane at –20° (oils and subsequently solidifies). An analytical sample melted at 43.4–45.0°.

Anal. Calcd for $C_{10}H_{20}O_4Si$: C, 51.70; H, 8.68. Found: C, 51.95; H, 8.70.

1,1-Dimethylsila-5-cyclooctanone (15).—A sample of dimethyldi(3-carboxypropyl)silane (4.5 g, 0.019 mole) was dissolved in 10 ml of hot 95% ethanol and neutralized with 20% sodium hydroxide solution. A solution of 3.6 g (0.0097 mole) of thorium chloride was prepared, and the two solutions were then mixed dropwise, with stirring into a 100-ml beaker. The gelatinous precipitate which formed was allowed to stir for several hours to

(11) The first preparation of this compound was reported by Dr. T. V. Liston. See T. V. Liston, Ph.D. Thesis, Purdue University, 1960.

(12) "Handbook of Chemistry and Physics," R. C. Weast, Ed., 45th ed, The Chemical Rubber Co., Cleveland, Ohio, 1964, p C-229.

permit coagulation, and was then filtered off and washed with water. Evacuation at 1 mm over potassium hydroxide for 24 hr afforded 5.6 g (84%) of the dry salt.

Dry distillation of the salt was carried out in a 25-ml distillation flask whose side arm was connected to two ice-water traps in series. A plug of glass wool was placed in the neck of the flask to prevent solid from leaving the bulb. The pressure in the system was slowly reduced to *ca.* 1 mm, and the flask was heated with a Wood's metal bath. Decomposition began at about 370°, and the bath was maintained between 400 and 500° for 1 hr. There was obtained 1.4 g of brownish liquid which was subjected to vpc collection (12-ft Apiezon L, 170°) to give 200 mg (7%) of the silacyclooctanone as a clear liquid. The ketone (n_D^{26} 1.4754) was the only major component of the mixture produced in the pyrolysis. It exhibited a carbonyl absorption (neat liquid, Perkin-Elmer Model 421 spectrophotometer) at 1701 cm^{-1} .

Anal. Calcd for $\text{C}_9\text{H}_{18}\text{OSi}$: C, 63.47; H, 10.65. Found: C, 63.39; H, 10.57.

The 2,4-dinitrophenylhydrazone prepared from this ketone melted at 134.5–135.0° (softened at 132°).

Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{N}_4\text{O}_5\text{Si}$: C, 51.41; H, 6.33; N, 15.99. Found: C, 51.59; H, 6.30; N, 16.02.

1,1-Dimethyl-6-hydroxysila-5-cyclononane (16) and 1,1-Dimethylsila-5-cyclononanol (17).—A 200-ml Morton flask was equipped as in the preparation of acyloin **7**, and the same preliminary steps were observed. The charge to the flask was 120 ml of toluene and 6.0 g (0.26 g-atom) of sodium. Addition of 6.8 g (0.026 mole) of dimethyldi(3-carbomethoxypropyl)silane in 30 ml of toluene was carried out over 7.5 hr. During this time sodium began to adhere to the walls of the flask and three further portions (*ca.* 3 g each) were intermittently introduced.

The reaction was stirred for 45 min after the last of the diester was added, and then hydrolyzed by adding 25 ml of methanol followed by 60 ml of 1:1 sulfuric acid–water. Sodium was still present in the reaction mixture when the latter was added, and evidently resulted in partial reduction of the acyloin (*vide infra*). Work-up as usual gave 2.4 g (47%) of material which boiled at 79–94° (0.4 mm), and was shown by vpc analysis (4-ft Apiezon L, 160°) to be a mixture of two compounds in an approximate ratio of 2:3 (in order of elution). The first of these was identified as 1,1-dimethylsila-5-cyclononanol.

Anal. Calcd for $\text{C}_{10}\text{H}_{22}\text{OSi}$: C, 64.45; H, 11.90. Found: C, 65.15; H, 12.05.

The 3,5-dinitrobenzoate prepared from this alcohol melted at 62.0–63.0°.

Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}_6\text{Si}$: C, 53.67; H, 6.36; N, 7.37. Found: C, 53.55; H, 6.44; N, 7.29.

The major product of the cyclization reaction was found to be unstable to vpc. When the material was subjected to gas chromatography on a 4-ft stainless steel Apiezon L column in conjunction with a glass-lined injection port, decomposition was minimized. A sample collected under these conditions afforded a correct analysis for 1,1-dimethyl-6-hydroxysila-5-cyclononane.

Anal. Calcd for $\text{C}_{10}\text{H}_{20}\text{O}_2\text{Si}$: C, 59.95; H, 10.06. Found: C, 60.11; H, 10.09.

The semicarbazone of this acyloin melted at 171.5–172.0°.

Anal. Calcd for $\text{C}_{11}\text{H}_{22}\text{N}_2\text{O}_2\text{Si}$: C, 51.33; H, 9.01; N, 16.33. Found: C, 51.49; H, 9.21; N, 16.20.

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Lactone Trimer of Dimethylketene

R. DONALD CLARK

Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee

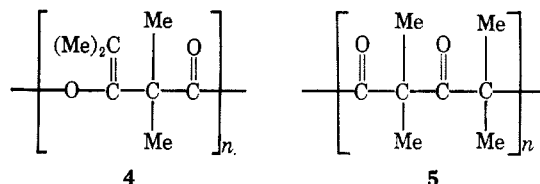
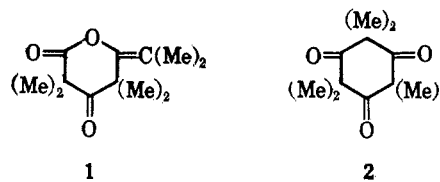
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A new trimer of dimethylketene, 5-hydroxy-2,2,4,4,6-pentamethyl-3-oxo-5-heptenoic acid δ -lactone (**1**), is reported. The mechanism of its formation is discussed, and new proposals are set forth to rationalize more completely the observed base-catalyzed reactions of dimers of dimethylketene.

Both β -lactone and cyclobutane dimers of ketene,¹ alkylketenes,² and dialkylketenes^{3,4} have been prepared. Various trimers, tetramers, and polymers of these ketenes have also been prepared. A stable trimer of dimethylketene, 2,2,4,4,6,6-hexamethyl-1,3,5-cyclohexanetrione (**2**), is formed by base-catalyzed reactions of dimethylketene, its dimers, or its polymers.^{5,6} The present paper concerns the formation of a less stable trimer of dimethylketene, 5-hydroxy-2,2,4,4,6-pentamethyl-3-oxo-5-heptenoic acid δ -lactone (**1**) by base-catalyzed disproportionation of the β -lactone dimer of dimethylketene, 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid β -lactone (**3**).

In the absence of labile hydrogen atoms, **3** reacts with strong base such as a sodium alkoxide to form an enolate anion.⁷ With less than equivalent amounts of

base, other products are formed. Although many products may be postulated, for simplicity the discussion will be limited to those four that are shown below.



Compounds **1**, **2**, and **4** have been found. Polymer conceivably is formed from **3** by a simple ring opening, like that with β -propiolactone, except that propagation is through the enolate anion rather than the carboxylate anion. Reaction at the oxygen atom of the enolate

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