TABLE I

S,S'''-BIS(2-AMINOETHYL) S',S''-ALKYLENE BISDITHIOCARBONATE DIHYDROHALIDES

Compound	Crude yield, %	M.p.,[a] °C.	ν_{max}^{KBr}, cm.$^{-1}$		Formula	C, %		H, %		S, %	
			C=O[b]	S-C-S[b]		Calcd.	Found	Calcd.	Found	Calcd.	Found
IVa	57	184–185 dec.	1645	875	$C_7H_{14}N_2O_2S_4\cdot 2HCl$	23.39	23.51	4.49	4.64	35.69	35.5
IVb	63	240–241 dec.	1640	880	$C_8H_{16}N_2O_2S_4\cdot 2HBr$	20.78	20.94	3.92	3.59	27.74	27.8
IVc	59	215–216 dec.	1650	875	$C_9H_{18}N_2O_2S_4\cdot 2HCl$	27.90	28.06	5.20	5.46	33.10	33.1
IVd	51	210–211 dec.	1650	875	$C_{10}H_{20}N_2O_2S_4\cdot 2HCl$	29.91	29.86	5.52	5.49	31.94	32.1
IVe	55	197–199 dec.	1650	875	$C_{11}H_{22}N_2O_2S_4\cdot 2HCl$	31.79	31.94	5.82	5.70	30.87	30.6

[a] Varied widely with rate of heating, typical values being reported. [b] Strong absorption; *cf.* ref. 4.

1,3-Dithiolan-2-ylidenedimethylammonium Bromide (VIII).—A solution of sodium dimethyldithiocarbamate hemihydrate[12] (4.00 g., 26.3 mmoles) in methanol (75 ml.) was added dropwise to a solution of 1,2-dibromoethane (4.5 ml., 53 mmoles) in the same solvent (10 ml.) over a period of 15–20 min. The reaction mixture was then stirred for 3 hr., maximum temperature being 31°. The methanol was removed under reduced pressure and the residual yellow solid was triturated in chloroform (100 ml.). The insolubles were removed by filtration, and the filtrate was evaporated to dryness under reduced pressure. The white residue after trituration in benzene was dried *in vacuo* at 63° over phosphorus pentoxide, yielding 3.86 g. (64%) of VIII, m.p. 174° (Kofler Heizbank). The same product was obtained from 1-bromo-2-chloroethane, sodium chloride having precipitated from the reaction mixture. The analytical sample was obtained as white prisms, m.p. 174°, by recrystallization from acetonitrile; λ_{max} in mμ ($\epsilon \times 10^{-3}$): 249 (12.2) at pH 1, 249 (12.7) at pH 7, 250 (13.3) in methanol; ν_{max}^{KBr} 1595 cm.$^{-1}$ (C=N, strong). The product isolated was the same when the ratio of dihalide to dithiocarbamate was varied from 1:1 to 4:1, and also when the reaction temperature was increased to 66° by external heating.

Anal. Calcd. for $C_5H_{10}BrNS_2$: C, 26.32; H, 4.42; N, 6.14. Found: C, 26.48; H, 4.59; N, 6.24.

***S,S′*-Bis(2-aminoethyl) 1,4-Butanebisthiosulfonate Dihydrobromide (IX)**.—Crude 1,4-butanedisulfonyl chloride[13] (m.p. 76–77°, 17.8 g., about 70 mmoles) was added in portions over a 30-min. period to a cold and well-stirred aqueous solution (100 ml.) of sodium hydroxide (11.2 g.) that had been saturated with hydrogen sulfide at 15°. The resulting mixture was stirred at 5° for 2 hr., the pH changing from 11 to 5, and at room temperature for 4 hr., the pH being maintained at 8 by the addition of 0.2 *N* sodium hydroxide solution (total about 30 ml.). A small amount of solid was removed by filtration, and the filtrate was evaporated to dryness under reduced pressure. The residual solid was extracted with *N,N*-dimethylformamide, first with four 50-ml. portions at room temperature and then with three 50-ml. portions hot. Evaporation *in vacuo* of the combined extracts left a yellow solid, which was rendered white by trituration in 2-propanol. The yield of crude disodium 1,4-butanedbisthiosulfonate (20.0 g.) was nearly quantitative.

To a well-stirred suspension of crude disodium 1,4-butanebisthiosulfonate (6.5 g., about 20 mmoles) in *N,N*-dimethylformamide (30 ml.) was added a solution of 2-bromoethylamine hydrobromide (8.61 g., 42.0 mmoles) in the same solvent (20 ml.). The resulting solution was heated at 80–90° for 5 hr. and evaporated to dryness under reduced pressure, the evaporation being repeated several times after successive additions of ethanol. The solid residue was extracted with three 50-ml. portions of methanol to remove sodium bromide, and the methanol-insoluble solid was dried *in vacuo* (8.03 g.). A solution of the crude product in water (100 ml.) was treated with Norit and evaporated to dryness *in vacuo*. Trituration of the white crystalline residue with two 25-ml. portions of methanol left 6.18 g. of IX, m.p. 177–178° dec. An additional 1.30 g., m.p. 176–177° dec., was obtained from the methanol washings, the total yield being about 75%. For analysis a small sample was recrystallized from methanol-ether (m.p. 171–172° dec.).

Anal. Calcd. for $C_8H_{20}N_2O_4S_4\cdot 2HBr$: C, 19.28; H, 4.45; S, 25.74. Found: C, 19.55; H, 4.52; S, 25.7.

***S,S′*-Bis(2-ureidoethyl) 1,4-Butanebisthiosulfonate (X)**.—To a stirred solution of *S,S′*-bis(2-aminoethyl) 1,4-butanebisthiosulfonate dihydrobromide (IX, 2.7 g., 5.5 mmoles) in water (50 ml.) was added dropwise a solution of potassium cyanate (0.89 g., 11 mmoles) in the same solvent (25 ml.). After about 15 min. the solution became cloudy, and solid began to precipitate. The mixture was stirred overnight at room temperature; the solid was collected, washed with water, and dried *in vacuo* over phosphorus pentoxide, yielding 1.8 g. (79%) of crude X, m.p. 177–179° dec. with predarkening. The crude product was recrystallized from water in 84–92% recovery and dried as described above, m.p. 183–184°.

Anal. Calcd. for $C_{10}H_{22}N_4O_6S_4$: C, 28.42; H, 5.25; N, 13.25. Found: C, 28.44; H, 5.21; N, 13.27.

***S*-2-Ureidoethyl 2-Ureidoethanethiosulfonate (XI)**.—A solution of potassium cyanate (0.811 g., 10.0 mmoles) in water (5 ml.) was added dropwise to a stirred solution of *S*-2-aminoethyl 2-aminoethanethiosulfonate dihydrochloride[14,15] (1.28 g., 5.00 mmoles) in water (10 ml.). The resulting solution was stirred at room temperature for 5 hr. and then evaporated to dryness under reduced pressure (oil pump) at room temperature, the evaporation being repeated several times after successive additions of methanol. The solid residue was extracted with three 5-ml. portions of *N,N*-dimethylformamide and the combined extracts were evaporated to dryness *in vacuo* at less than 50°. Evaporations were again repeated after successive additions of methanol until the oily residue solidified. Recrystallization from ethanol (100 ml.) gave crude XI as a cream-colored solid, which was dried *in vacuo* (0.62 g., m.p. 115–117° dec. with presoftening). Analytically pure XI, m.p. 151–153° dec., was obtained by diluting a Norit-treated solution of the crude product (250 mg.) in warm methanol (10 ml.) with an equal volume of ether. The recovery (108 mg.) corresponded to an over-all yield of 20%.

Anal. Calcd. for $C_6H_{14}N_4O_4S_2$: C, 26.65; H, 5.22; S, 23.72. Found: C, 26.81; H, 5.25; S, 23.9.

The yield was little improved when the above described procedure was repeated on a 25-mmole scale with omission of the initial ethanol recrystallization. The product, twice recrystallized from 1:1 methanol–ether, melted at 145–146° dec.

Acknowledgment.—The authors are indebted to Mrs. T. N. Carruthers, Jr., and Mr. G. S. McCaleb for preparation of VIII, and to Dr. W. J. Barrett and associates of the Analytical Section of this institute for microanalyses and spectra.

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The Preparation of Hexaphenylcyclotrisilthiane and of Tetraphenylcyclodisilthiane[1]

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In the course of investigations on the displacement of halogen or amino groups on silicon with sulfhydryl or $-S-SiR_3$ groups, two cyclosilthianes, I and II, have

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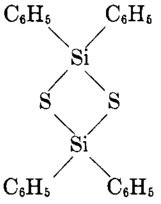
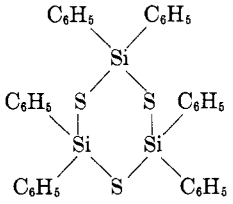


I



II

been prepared. A compound with the structure I melting at 145–147° has been reported.[2] Tetraphenylcyclodisilthiane (I) prepared in this work by pyrolysis of II melted at 163–165°. Hexaphenylcyclotrisilthiane (II) has been unreported previously.

The cyclic trimer II was prepared in 55% yield by the reaction of hydrogen sulfide with diphenyldichlorosilane in benzene solution containing a 2:1 mole ratio of pyridine to the silane. Repeated attempts to isolate I from the reaction mixture have been unsuccessful. Compound II was a colorless crystalline solid melting sharply at 188–189°. Elemental analyses and experimentally determined molecular weights were in reasonable agreement with the calculated values. Further, compound II contained no halogen and no hydrogen active in the Zerewitinoff determination and was therefore formulated as cyclic. The molecular weight of II (Table I) was determined by three methods since this compound is being used in attempts to prepare higher molecular weight linear silthiane polymers by ring opening with subsequent reaction.

TABLE I

MOLECULAR WEIGHT DETERMINATIONS

Compound	Formula	Calcd.	Concn., mole/l. in benzene	Exptl. method, found Cryoscopic	Isopiestic	V.p. osmometric
Dimer I	$C_{24}H_{20}S_2Si_2$	428	0.030			383
			0.120			389
			0.100	391[a]		
Trimer II	$C_{36}H_{30}S_3Si_3$	642	0.026			651
			0.074			626
			0.157			632
			0.100	595[a]		
			0.041		653	

[a] Average of five determinations.

Pyrolysis of II in a glass tube at reduced pressure resulted in collection of a crystalline solid in the upper cool part of the tube. Elemental analyses, molecular weight determinations, and infrared spectra support the proposal that I is a cyclic dimer. No material melting near the 145–147° value reported by Moody[2] was isolated. It is possible that I is a crystalline modification of Moody's compound. Polymorphism is common among the corresponding cyclic siloxanes.[3] A mixture melting point of I with II resulted in depression.

The tetramethyl analog of I, tetramethylcyclodisilthiane, has been prepared by thermal rearrangement of hexamethylcyclotrisilthiane.[4] Yokoi[5] has determined bond lengths and angles for these compounds by electron diffraction, and Kriegsmann and Claus[6] have investigated their vibrational spectra and structures.

Young and co-workers[7] have been particularly interested in using infrared data to distinguish ring sizes in various substituted cyclosiloxanes. They have shown that compounds containing six-membered siloxane rings (cyclic trimers) can be distinguished from similarly substituted eight-membered cyclic siloxanes by a characteristic shift in infrared absorption. Our somewhat comparable results with the four- and six-membered cyclic silthianes (I and II) show that vibrational absorption spectra of both have identical bands except for a single shift from 13.45 μ for the dimer I to 13.63 μ for the trimer II. The six-membered cyclosiloxane ring shows a strong band at 9.8–9.9 μ. It is not unreasonable, when one considers the differences in force constants and reduced masses existing with Si–O and Si–S bonds, that the strong absorption of II at 13.63 μ may be characteristic of a six-membered cyclosilthiane ring.

X-Ray powder photographs for I and for II show distinctly different patterns which strongly suggest different compounds (see Table II). The unit cells in each case are large, and the crystal habit for each is probably monoclinic.

TABLE II

X-RAY DIFFRACTION MEASUREMENTS

Compound	Principle X-ray powder photograph lines Distance, Å.	I (rel.)
Dimer I	9.87	vs
	8.30	m
	6.62	ms
	6.15	m
	4.99	s
	4.72	ms
	4.44	m
	4.25	m
	4.09	mw
	3.54	m
Trimer II	9.60	vs
	8.54	s
	6.83	m
	5.79	ms
	5.21	m
	4.79	m
	4.43	mw
	4.26	m
	3.73	ms

Experimental[8]

Hexaphenylcyclotrisilithiane (II).—In a 1-l. three-neck flask fitted with a thermometer, gas introduction tube, magnetic stirrer, dropping funnel, and reflux condenser was placed 100 ml. of dry benzene and 22.9 g. (0.29 mole) of anhydrous pyridine. The flask was flushed with nitrogen and subsequently anhydrous hydrogen sulfide was bubbled slowly into the solution while redistilled diphenyldichlorosilane (31.63 g., 0.125 mole) was added drop by drop over a period of 0.5 hr. The temperature rose to

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(8) Elemental analyses were performed by Elek Microanalytical Laboratories, Torrance, Calif. 90502. All melting points are corrected. Infrared spectra were run on a Baird-Atomic Model KM-1 recording spectrophotometer.

45° during the addition. When the silane introduction was complete, an additional 150 ml. of benzene was added and the temperature was maintained at 50–55° for 2 hr. while slow introduction of hydrogen sulfide was continued. The mixture was filtered from precipitated pyridine hydrochloride in a drybox, the residue was washed once with 50 ml. of hexane (dried over Na), and the wash liquid was combined with the filtrate. Material volatile to 240° was distilled from the filtrate. The pot residue was dissolved in 150 ml. of boiling hexane plus a minimum amount (about 40 ml.) of benzene, filtered, and allowed to cool and crystallize. A total of 11.2 g. of II (m.p. 186–188°) was obtained. A second crop (3.5 g., m.p. 186–188°) was separated by partial concentration of the mother liquor. Total yield of II was 55%. II consisted of colorless, well-formed crystals of density 1.271 g./ml.; infrared bands (KBr pellet) were at 7.00, 9.01, 10.01, 13.63, 14.08, and 14.38 μ.

Anal. Calcd. for $C_{36}H_{30}S_3Si_3$; C, 67.29; H, 4.67; S, 14.96; Si, 13.08. Found: C, 67.35; H, 4.62; S, 14.40; Si, 12.90.

Failure to heat the reaction mixture after introduction of the silane resulted in reduced yields. II was only slowly hydrolyzed by atmospheric moisture, the melting point dropping only 4° after 2 days' standing in an open container in an air-conditioned laboratory.

Tetraphenylcyclodisilithiane (I).—Into a 30 × 2.5 cm. Pyrex tube connected at the top by a ground glass joint to a cold-finger trap cooled by a Dry Ice–ether slurry and then to an oil pump was placed 2.70 g. (0.004 mole) of II. The tube was suspended to a depth of 10 cm. in an electric furnace, the internal pressure was reduced to less than 1 mm., and heating was maintained at 300–315° for 2 hr. During this period, a tan crystalline solid sublimed to the cool upper walls of the tube. This solid was crystallized from 20 ml. of a hexane–benzene mixture (20% benzene by volume). Recrystallization from the same solvent gave 1.40 g. of colorless crystalline I (m.p. 163–165°; density, 1.268 g./ml.). The yield was 52% based on starting II. Remaining in the tube was 0.25 g. of a viscous glass, while 0.3 g. of an unidentified liquid was collected in the cold finger; infrared bands (KBr pellet) were at 7.00, 8.99, 10.01, 13.45, 14.04, and 14.35 μ.

Anal. Calcd. for $C_{24}H_{20}S_2Si_2$: C, 67.29; H, 4.67; S, 14.96; Si, 13.08. Found: C, 65.96; H, 4.88; S, 14.42; Si, 14.43.

A reduced yield of I (about 25%) resulted when the pyrolysis was carried out at atmospheric pressure. Admixture of I with an equal weight of II produced a material with a melting range of 149–171°.

Molecular Weight Determinations.—Molecular weights (Table I) of I and II were determined in benzene using both standard cryoscopic techniques and vapor pressure osmometric equipment.[9] In addition, the molecular weight of II was determined by the isopiestic procedure described by Childs[10] using azobenzene as the reference compound.

X-Ray Diffraction Measurements.—Table II lists principle X-ray powder photograph lines and intensities for the dimer I and the trimer II. Cu Kα radiation (Ni filter) was used. Both samples of I and II were recrystallized from a 3:1 mixture of hexane and benzene.

Acknowledgment.—The authors are indebted to Dr. Elihu Goldish for the X-ray diffraction photographs and interpretation and to Dr. John Stern, who built the vapor pressure osmometer.

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The Synthesis and Thermal Decomposition of 3,3,6,6-Tetramethyl-1,4-cyclohexadiene

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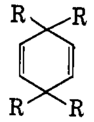
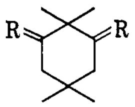
The many unusual properties[1] and reactions[2–10] of norbornadiene (I) have led us to examine other compounds having parallel nonconjugated but interacting double bonds. The simplest hydrocarbon with this structural feature is 1,4-cyclohexadiene (II), which, like I, has an ultraviolet absorption spectrum indicative of interacting π-electron systems.[1,11] Since the chemistry of II is complicated by double-bond isomerization[12] and dehydrogenation to benzene,[13] we decided to synthesize 3,3,6,6-tetramethyl-1,4-cyclohexadiene (III).

Methylation of dimedone[14] gave 2,2,5,5-tetramethylcyclohexane-1,3-dione (IV), which was reduced to a mixture of diols (V) by lithium aluminum hydride and then converted to a crystalline diacetate (VI), m.p. 64–65°,[15] by reaction with acetic anhydride. When pyrolyzed at 350°, the diacetate VI was 10% decomposed and yielded two volatile products, A and B, in a ratio of 10:1, respectively. Pure A, m.p. 7–8°, was obtained by preparative vapor phase chromatography and was identified as III by spectroscopic methods. The infrared and n.m.r. spectra and the v.p.c. retention time of product B proved to be identical with those of authentic p-xylene.

I



II, R = H
III, R = CH_3



IV, R = O
V, R = H, OH
VI, R = H, $OCOCH_3$

The infrared absorption spectrum of III exhibits a very strong vinyl hydrogen deformation absorption at 764 cm.$^{-1}$. The corresponding absorption for II is found at a much lower frequency (678 cm.$^{-1}$). The shift may be due to the extensive allylic substitution in III.[16]

The n.m.r. spectrum of III is particularly instructive in that two sharp resonance signals are observed at τ 4.7 and 9.0, with an area ratio of 1:3.1.

The most abundant peaks in the mass spectrum of III are listed in Table I. We tentatively assign the two intense peaks, having m/e of 121 and 105, to the relatively stable 1,1,4-trimethylbenzenonium ion[17] and the methyltropylium ion, respectively.

In contrast to the broad envelope of absorption bands

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[17] According to the nomenclature of W. von E. Doering, M. Saunders, H. Boynton, H. Earhart, E. Wadley, W. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958).