TABLE I

COMPLEX METAL HYDRIDE REDUCTIONS OF 3,3,5 TRIMETHYLCYCLOHEXANONE (I) AND 4-*t*-BUTYLCYCLOHEXANONE (II)

Entry	Reagent	Solvent	Temp., °C.	Molar ratio, metal hydride to ketone I	% Axial alcohol from I (normalized)	% Unreduced ketone I	Molar ratio, metal hydride to ketone II	% Axial alcohol from II (normalized)	% Unreduced ketone II
1[a]	LiAlH$_4$	Et$_2$O	30	1.1[a]	55[a]	2.6[a]	1.2	8	<1
2	LiAlH$_4$	Et$_2$O	0	1.3	58	<1	1.2	7.5	<1
3	LiAlH$_4$	Et$_2$O	−40	1.1	61.5	<1	1.0	5	2.6
4	LiAlH$_4$[b]	C$_5$H$_5$N	27	1.0	71	<1	1.1	11.5	<1
5a	LiAlH$_4$	C$_5$H$_5$N	0	1.05	75	<1	1.7	10.5	<1
[b]	LiAlH$_4$	C$_5$H$_5$N	0	0.77	74	1.3	...	...	...
[c]	LiAlH$_4$	C$_5$H$_5$N	0	0.50	76	0.8	...	...	...
[d]	LiAlH$_4$	C$_5$H$_5$N	0	0.30	76	41.3	...	...	...
6	LiAlH$_4$	C$_5$H$_5$N	−40	1.05	83	<1	1.1	8.5	30
7	LiAlH$_4$	THF	65	0.38[a]	74[a]	7[a]	...	...	...
8	LiAlH$_4$	THF	27	1.2	76.5	<1	1.2	8	<1
9	LiAlH$_4$	THF	0	1.3	82	<1	2.0	7.5	<1
10	LiAlH$_4$	THF	−40	1.1	87.5	<1	2.0	4.0	<1
11	NaBH$_4$	CH$_3$OH	27	1.2	80.5	<1	1.2	20	<1
12	NaBH$_4$	CH$_3$OH	0	1.3	86	<1	2.0	16.5	<1
13	NaBH$_4$[c]	CH$_3$OH	−40	1.2	98	<1	1.3	12.0	2
14	NaBH$_4$[d]	CH$_3$OH	−70	1.2	98	27.4	...	...	...
15	NaBH$_4$	*i*-C$_3$H$_7$OH	27	1.4	57.5	<1	1.4	12.5	<1
16	NaBH$_4$	*i*-C$_3$H$_7$OH	0	1.4	62.0	<1	1.5	13.0	<1

[a] Results taken from ref. 1. [b] There is no opportunity for lithium tetrakis(N-dihydropyridyl)aluminate to play a significant role in these reductions since it is slowly formed under these conditions and reduces dialkyl ketones only with great difficulty (P.T. Lansbury and J. O. Peterson, *J. Am. Chem. Soc.*, **83,** 3537; **84,** 1756 (1962)). The present reductions were accomplished within a few minutes by addition of lithium aluminum hydride to pyridine solutions of I and II. [c] Although NaBH(OCH$_3$)$_3$ may be involved at 0° and 27°, there was very little hydrogen evolution at −40° and none at −70°, so one may consider solvated sodium borohydride to be the major reducing species. [d] Since large amounts of ketone remain unchanged under these conditions it is conceivable that some reduction might occur during work-up. This possibility was shown to be extremely remote since a semiquantitative kinetic run at −75°, using the usual work-up for each aliquot taken, showed that good second-order kinetics were obeyed (k_2 = 6.7 × 10^{-4} l./mole-sec.) when the data were treated by the method of Brown, *et al.*, *Tetrahedron*, **1,** 214 (1957).

whereas several of the reductions at −40° did not proceed to completion in the allotted time. When the reducing agent was lithium aluminum hydride, the excess hydride was neutralized with methanol at the temperature at which the reduction was run before continuing with the work-up. The reaction mixtures were then poured into a mixture of ice, water, and ether and acidified with dilute hydrochloric acid. The crude product was taken up in ether, washed with sodium bicarbonate solution, saturated salt solution, and dried over anhydrous sodium sulfate. The ether solution was concentrated and the mixtures of *cis*- and *trans*-3,3,5-trimethylcyclohexanols and *cis*- and *trans*-4-*t*-butylcyclohexanols were analyzed by gas–liquid partition chromatography using an F & M Model 300 programmed temperature–gas chromatograph. Peak areas were calculated from the product of the peak height and half-height width.

Synthetic mixtures of the pure *cis*- and *trans*-3,3,5-trimethylcyclohexanols, as well as mixtures of the alcohols and I were prepared and analyzed by gas chromatography. Since experimental and calculated results agreed within ±1%, no correction factors were used. The separation was carried out on a 5-ft. column freshly prepared using 20% by weight of the benzene extract from commercial "Tide" detergent on Chromosorb P. Helium flow rate was approximately 120 ml. per min. and the temperature was programmed from 90° at a rate of 4.6° per minute. The ketone had a retention time of 7.67 min., the *trans* alcohol 10 min., and the *cis* alcohol 12.67 min.

Synthetic mixtures of pure *cis*- and *trans*-4-*t*-butylcyclohexanols were prepared and analyzed by gas chromatography in the same manner. The experimental results agreed with the calculated results within 1% in the absence of 4-*t*-butylcyclohexanone up to 20% of the ketone present in the mixture and within 2–3% up to 40% of the ketone in the mixture, the ketone partially masking the *cis* alcohol when it is present in large amounts. The separation was carried out on the same 5-ft. "Tide" column using a flow rate of approximately 200 ml. per min. The temperature was programmed from 90° at 4.6° per min. The retention time of the ketone was 13.5 min., that of the *cis* alcohol 14.67 min., and that of the *trans* alcohol 16.67 min.

The crude product mixtures from the hydride reductions were analyzed in the previous manner. The only peaks observed were those corresponding to the ether solvent, which immediately flashed off, the two alcohols and, in some cases where the reduction was incomplete, the ketones. In the table the yields of axial alcohols are normalized to 100%.

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The Preparation of Certain Cyclopolymethylenecyclosiloxanes

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The hydrolysis of organosilicon dihalides generally results in the formation of a mixture of cyclic and linear organopolysiloxanes with the latter predominating. A survey reveals that usually the hydrolysis involves the use of dialkyl, diaryl, or alkyl–aryl substituted dichlorosilanes. Siloxane polymers resulting from the hydrolysis of 1,1-dichloro-1-silacyclobutane and 1,1-dichloro-1-silacyclopentane have been described by Hersch.[1] This paper records the preparation and characterization of four crystalline polymers of the type [(CH$_2$)$_x$SiO]$_y$ where x is 4 or 5 and y is 3 or 4.

(1) J. M. Hersch, U. S. Patent 2,464,231 (1949).

Experimental

Tetracyclopentamethylenecyclotetrasiloxane.—To a vigorously stirred suspension of 20.7 g. (0.85 g.-atom) of magnesium powder in 400 cc. of anhydrous diethyl ether was added, dropwise, a mixture of 34.1 g. (0.20 mole) of silicon tetrachloride and 92.0 g. (0.40 mole) of 1,5-dibromopentane. After a few milliliters of the mixture had been added, the reaction was initiated using a small crystal of iodine. After addition, the mixture was heated for 3 hr. after which it was left standing overnight. Hydrolysis was effected by the cautious addition of 200 ml. of a 10% hydrochloric acid solution and the ether layer dried over anhydrous calcium chloride.

Distillation at low pressures yielded 17.5 g. of material, principally 1,5-dibromopentane. Using a steam heated condenser, a viscous oil was obtained of which three fractions were collected: (1) b.p. 156–169°; (2) b.p. 173–187°; (3) b.p. 198–200° (0.07 mm.). Fractions 1 and 2 crystallized at room temperature while the viscous oil in fraction 3 required longer time. The crystals from fractions 1 and 2 were recrystallized from hot 95% ethanol giving a white product, 3.6 g., m.p. 71–73°.

Anal. Calcd. for $C_{20}H_{40}O_4Si_4$: C, 52.58; H, 8.82; Si, 24.59; mol. wt., 457. Found: C, 53.17; H, 8.78; Si, 24.09; mol. wt., 452.

Infrared absorption: strong, 2910, 2855, 1068, 783 cm.$^{-1}$; medium, 1446, 1398, 1199, 1177 cm.$^{-1}$; weak, 1460, 1343, 1290, 1268, 1003, 856, 769 cm.$^{-1}$.

Tricyclopentamethylenecyclotrisiloxane.—Similarly, 33.3 g. (0.19 mole) of 1,1-dichloro-1-silacyclohexane in 250 ml. of anhydrous ether, was treated with 38.1 g. (2.12 moles) of crushed ice. The mixture was vigorously stirred and maintained at reflux for 1 hr. The ether layer was then washed with 50 ml. of water and again stirred at reflux with 50 ml. of a 5% solution of potassium hydroxide for an additional hour. The ether layer was washed once with 50 ml. of a 1% hydrochloric acid solution and twice with water, then dried over calcium chloride. Vacuum distillation, after release of the ether, yielded a material which crystallized in the condenser. This material, recrystallized from hot 95% ethanol, gave 2.4 g. of white crystals, m.p. 92–94°. The pot residue probably contained higher polycyclic compounds including the tetramer, as indicated by infrared data.

Anal. Calcd. for $C_{15}H_{30}O_3Si_3$: C, 52.58; H, 8.82; Si, 24.59; mol. wt., 343. Found: C, 52.99; H, 9.12; Si, 24.16; mol. wt., 335.

Infrared absorption: strong, 2910, 2850, 1016, 1000, 784 cm.$^{-1}$; medium, 1445, 1398, 1175, 905 cm.$^{-1}$; weak, 1460, 1341, 1289, 1267, 1197, 855, 765 cm.$^{-1}$.

Tricyclotetramethylenecyclotrisiloxane and Tetracyclotetramethylenecyclotetrasiloxane.—In similar manner, 20 g. (0.82 g.-atom) of magnesium powder suspended in 400 ml. of anhydrous ether was treated with 34 g. (0.20 mole) of silicon tetrachloride and 86 g. (0.40 mole) of 1,4-dibromobutane. After working up as before, and evaporation of the ether, 2.2 g. of a solid precipitated. This was filtered and recrystallized from hot heptane–octane mixture as fine white crystals, m.p. 199–201°, tricyclotetramethylenecyclotrisiloxane.

Anal. Calcd. for $C_{12}H_{24}O_3Si_3$: C, 47.95; H, 8.05; Si, 28.03; mol. wt., 301. Found: C, 48.18; H, 7.94; Si, 27.95; mol. wt., 292 (Rast).

Infrared absorption: strong, 2940, 2865, 1408, 1074, 1034, 1010 cm.$^{-1}$; medium, 1454, 1249, 855, 739, 705 cm.$^{-1}$; weak, 1307, 1190, 1157, 907, 788 cm.$^{-1}$; shoulder, 1467 cm.$^{-1}$.

The remaining oil was distilled yielding 1,4-dibromobutane, b.p. 61–64° (5.4 mm.), and an uncharacterized silicon-containing liquid, b.p. 43–52° (5.4 mm.), showing Si–H infrared absorption. Further distillation yielded a solid, 2.8 g., m.p. 114–116°, tetracyclotetramethylenecyclotetrasiloxane.

Anal. Calcd. for $C_{16}H_{32}O_4Si_4$: C, 47.95; H, 8.05; Si, 28.03; mol. wt., 401. Found: C, 48.17; H, 8.23; Si, 28.25; mol. wt., 415 (Rast).

Infrared absorption: strong, 2950, 2875, 1076, 1065 cm.$^{-1}$; medium, 1455, 1410, 1249, 1014, 855, 704 cm.$^{-1}$; weak, 1310, 1192, 1155, 817, 790, 740, 672 cm.$^{-1}$; shoulder, 1468, 1065 cm.$^{-1}$.

This synthesis was repeated by treating 31.0 g. (0.20 mole) of 1,1-dichloro-1-silacyclopentane in ether with 38.0 g. (2.10 moles) of crushed ice. After an hour of reflux, 95 ml. of a 5% potassium hydroxide solution was added and refluxing continued for another hour. The ether layer was then washed several times with 50-ml. portions of water and dried over anhydrous calcium chloride. Evaporation of ether gave 0.8 g. of a crystalline solid, m.p. 199–201°, and a second solid, m.p. 115–116°. Infrared data were identical on the products prepared by these two methods.

Infrared absorption data were obtained using a Perkin-Elmer Model 21, linear in wave number, spectrophotometer equipped with sodium chloride optics. Solution spectra were recorded, using carbon tetrachloride and carbon disulfide, to cover 4000–1300-cm.$^{-1}$ and 1300–650-cm.$^{-1}$ regions, respectively. All samples were run in a 0.08-mm. fixed thickness salt cell, uncompensated. Sample concentrations were as follows: 250 mg. of solute per 2.5 ml. of carbon tetrachloride and 50 mg. of solute per 2.5 ml. of carbon disulfide, with the exception of tricyclotetramethylenecyclotrisiloxane where solubility difficulties made it necessary to use approximately 95 mg. of sample per 2.5 cc. of carbon tetrachloride.

Preparation of Ornithine from Methyl 2,5-Diazidovalerate

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2,5-Dichlorovaleric acid is an attractive starting material for the synthesis of ornithine (2,5-diaminovaleric acid) because it can be prepared from carbon tetrachloride and ethylene followed by dehydrohalogenation, chlorination, and hydrolysis.[1-3] Direct ammonolysis of 2,5-dichlorovaleric acid gives the ring closed products proline and 2-tetrahydrofuramide[4] with no evidence for ornithine formation. In order to avoid these products, some source of nitrogen incapable of undergoing ring closure reactions is desirable for the synthesis of ornithine.

We have found that sodium azide displaces both chloro groups in methyl 2,5-dichlorovalerate to form methyl 2,5-diazidovalerate. Reduction followed by hydrolysis gave ornithine in 63% yield based on methyl 2,5-dichlorovalerate.

$$ClCH_2CH_2CH_2CH(Cl)COOCH_3 + NaN_3 \xrightarrow{(CH_3)_2SO_4} N_3CH_2CH_2CH_2CH(N_3)COOCH_3$$

$$N_3CH_2CH_2CH_2CH(N_3)COOCH_3 \xrightarrow[\text{2. } H_2O-HCl]{\text{1. } H_2-Pd\ C} H_2NCH_2CH_2CH_2CH(NH_2)COOCH_3 \cdot HCl$$

Methyl 2,5-dichlorovalerate was prepared using three moles of methanol and 2,2-dimethoxypropane[5] in the presence of Dowex 50-H$^+$. The reaction of methyl 2,5-dichlorovaleric acid and sodium azide goes smoothly in dimethyl sulfoxide at 60–65° and is 97.5% complete after five hours. Reduction of crude[6] methyl 2,5-di-

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(1) R. Joyce, W. Hanford, and J. Harmon, *J. Am. Chem. Soc.*, **70**, 2529 (1948).

(2) A. Nesmejanov, V. Kose, and R. Friedlina, *Dokl. Akad. Nauk, SSSR*, **103**, 109 (1955).

(3) For other routes to ornithine see D. M. Greenberg, "Amino Acids and Proteins," Charles C Thomas, Publisher, Springfield, Ill., 1951, p. 153; S. Akabori, Y. Itumi, and T. Okuda, *Nippon Kagaku Zasshi*, **77**, 490 (1956); *Chem. Abstr.* **52**, 8958*h* (1958); A. Nesmejanov, *et al.*, *Chem. Tech.*, **9**, 139 (1957).

(4) R. A. Strojny, H. C. White, and E. J. Strojny, *J. Org. Chem.*, **27**, 1240 (1962).

(5) N. Lorette and J. Brown, *ibid.*, **24**, 261 (1959).

(6) Methyl 2,5-diazidovalerate is a distillable liquid, b.p. 85–93° (0.3 mm.). The analysis of the distillate was low in nitrogen, perhaps because of loss of nitrogen during distillation.