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.

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

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

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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(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.

azidovalerate with hydrogen and 5% palladium on charcoal at 0–25° and atmospheric pressure was followed by hydrolysis to yield ornithine hydrochloride.

Experimental

Methyl 2,5-Dichlorovalerate.—A mixture of 2,5-dichlorovaleric acid (27.4 g., 0.16 mole), methanol (15.4 g., 0.48 mole), 2,2-dimethoxypropane (50 g., 0.48 mole), and a catalytic amount of dry, powdered Dowex 50-H$^+$ was stirred at room temperature for 20 hr. and heated at 40–60° for 24 hr. After removal of the catalyst by filtration, distillation of the brown solution gave 18.1 g. (61% yield) of ester, b.p. 72–73° (1 mm.). Vapor phase chromatography showed one peak and a trace impurity.

Anal. Calcd. for $C_6H_{10}O_2Cl_2$: C, 38.94; H, 5.45; Cl, 38.32. Found: C, 39.34; H, 5.67; Cl, 38.69.

DL-Ornithine Hydrochloride.—Methyl 2,5-dichlorovalerate (9.40 g., 0.05 mole) was added to a mixture of 50 ml. of dimethyl sulfoxide and 13.0 g. (0.20 mole) of sodium azide and stirred for 5 hr. at 60–65°. Water was added and the orange solution extracted with ether. An aliquot of the total aqueous portion was found to contain 97.5% of the theoretical amount of inorganic chloride on titration with silver nitrate. The ether solution was washed, dried, and evaporated under reduced pressure to yield a bright yellow liquid, presumably methyl 2,5-diazidovalerate.[6]

This product was taken up in 50 ml. of 95% ethanol and placed in a reduction flask equipped with a stirrer, a sintered glass sparger, and a gas outlet tube. One gram of 5% palladium on charcoal suspended in 50 ml. of ethanol was added. With ice cooling, hydrogen was bubbled in for 2 hr. A small amount of fresh catalyst and 8 ml. of concentrated hydrochloric acid were added and reduction allowed to continue for 1 hr. with ice cooling and 4 hr. at room temperature. Filtration, evaporation, and refluxing with 40 ml. of 5 *N* hydrochloric acid for 4 hr. yielded a brown solution which was evaporated and redissolved in water. Passage through a column containing 70 g. of Dowex 50-H$^+$ and washing with water until the eluate was chloride-free followed by elution with ammonia gave, on evaporation, a basic oil containing 65% of the theoretical amount of ornithine by hydrochloric acid titration. Addition of hydrochloric acid to pH 3.8 and evaporation gave a tan-colored oil which, on trituration with absolute methanol, yielded 5.8 g. (63% of theory) of DL-ornithine hydrochloride. An 85% recovery of white crystals containing 98.2% of the theoretical amount of chloride ion was obtained on recrystallization from water–ethanol. Comparison of our product with an authentic sample of DL-ornithine hydrochloride showed them to possess identical infrared and n.m.r. spectra and identical R_f values on paper chromatography of 0.03 in collidine–water (125:44) and 0.09 in *n*-butyl alcohol–acetic acid–water (40:10:50).

Hydrogen Bonding in Pyrrylmethenes[1]

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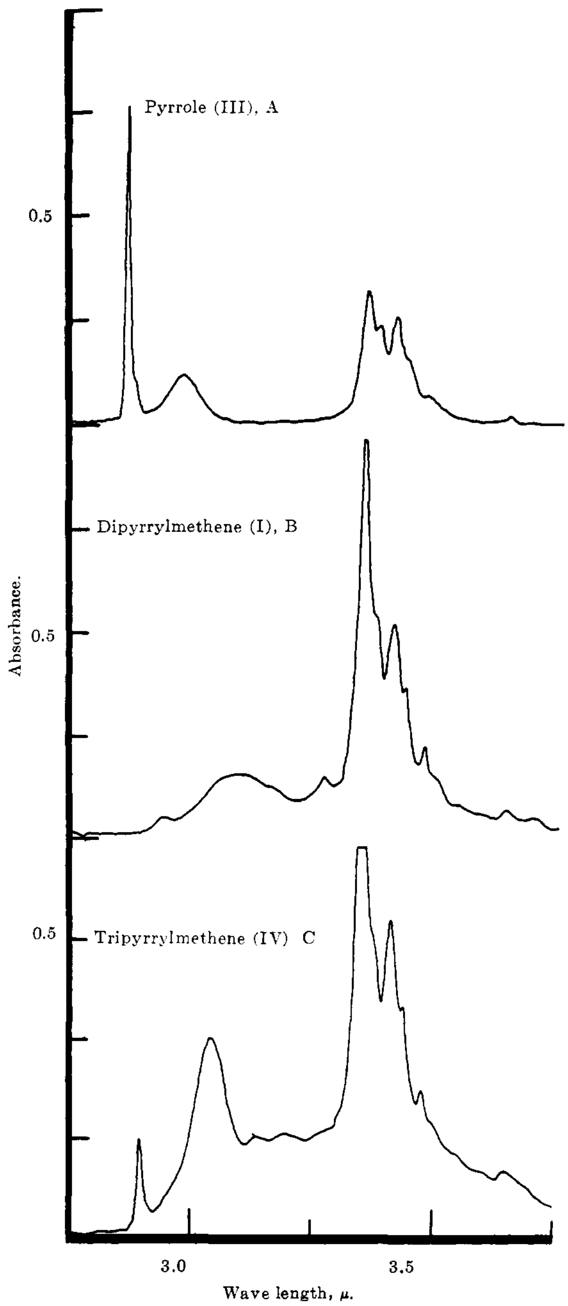
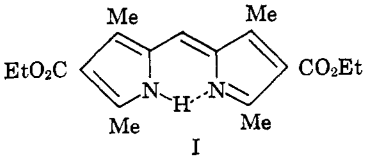


Fig. 1.—Infrared spectra in carbon tetrachloride. Letters (A, B, and C) refer to solutions marked in Table I.

Some time ago Vestling and Downing[3] presented infrared spectral evidence for hydrogen bonding in 2,2′-(3,3′,5,5′-tetramethyl-4,4′-diethoxycarbonyl)dipyrrylmethene (I) and in the 3,4′,5-trimethyl-3′,4-diethoxycarbonyl-5′-bromo analog (II), both in carbon tetrachloride. The absence of dilution studies prevented a decision between intermolecular hydrogen bonding and an intramolecular bonding as presented for I. A proposal of the latter type has been made independently by Brunings and Corwin[4] from other considerations and such structures have been assumed[5] *a priori*, although in fact this had not been established at



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[2] National Science Foundation Undergraduate Participant (NSF-G21628).

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