disproportionation *in vacuo* according to the equation $5Si_2Cl_6 \rightarrow 4SiCl_4 + Si_6Cl_{14}$.

In a representative reaction 1.4540 g. (5.45 mmoles) of pure disilicon hexachloride and less than 0.10 mmole of trimethylamine were placed together in a sealed evacuated vessel and allowed to stand at room temperature for twelve hours. A liquid and large clear cubic crystals now were present in the tube. The tube then was cooled to −45°, opened to a vacuum system and the material volatile at that temperature and 10^{-5} mm. of pressure was removed, measured and identified as 3.14 mmoles of $SiCl_4$. The large clear crystals remaining in the tube were allowed to warm to 0° where an equilibrium pressure of 12.3 mm. was observed. The material volatile at 0° and 10^{-5} mm. of pressure then was removed, measured and identified as 1.12 mmoles of $SiCl_4$.

The white microcrystalline solid remaining in the tube had the composition $(Si_{1.00}Cl_{2.36})_x$, and was heated gradually to 125° with the pressure maintained at 10^{-5} mm. At this temperature and pressure the entire solid residue sublimed and condensed into beautiful clear crystals, which upon standing at room temperature gradually reverted to the microcrystalline solid previously described; 0.7419 g. of this solid was dissolved in trichlorosilane and the data shown in Table I were obtained.

TABLE I

	SiHCl₃				
° C.	Vapor pressure in mm.	Mmoles of[3]	Vapor tension of solution in mm.	ΔP_{mm}	Mmoles of solute
0.00	219.0	59.6–1.1	215.0	4.0	1.09
0.00	219.0	50.7–1.1	214.2	4.8	1.11
5.53	277.0	50.2–1.1	270.8	6.2	1.12

From the tabulated data the apparent molecular weight of the white solid is found to be 668 ± 7[4]; calculated for Si_6Cl_{14}, 664.8.

Analysis of a sample purified by recrystallization from trichlorosilane and vacuum sublimation gave: 25.16% Si, 74.54% Cl. Calculated for Si_6Cl_{14}: 25.33% Si, 74.67% Cl.

In vacuo, Si_6Cl_{14} reacts slowly with methanol with the evolution of 4.92 moles of hydrogen per mole.

Traces of trimethylamine catalyze further disproportionation of Si_6Cl_{14} at elevated temperatures to $SiCl_4$ and a yellow solid, $(Si_{1.00}Cl_{1.80})_x$, different from any "sub-chloride" reported by earlier workers.[5,6,7,8,9] The temperature at which the rate of this disproportionation becomes measurable depends on the amount of amine present.

Si_6Cl_{14} apparently is polymorphic with a phase transition occurring at temperatures from 100 to 250° from a low temperature microcrystalline form to a cubic crystalline form. The temperature at which this occurs depends upon the rate of heating. The high temperature form melts sharply at 318 ± 3° with no measurable decomposition.

Si_6Cl_{14} is soluble in, and can be recovered unchanged from, trichlorosilane and diethyl ether. It is insoluble in benzene, CCl_4, $Cl_2CF–CF_2Cl$, and methylcyclohexane.

Differences in properties between the Si_6Cl_{14} prepared in the present synthesis and substances of this composition reported by earlier workers,[10,11,12] may be accounted for by the apparent isomeric purity of the present compound and the fact that exposure to traces of oxygen materially reduces the thermal stability of Si_6Cl_{14}.

(3) The amount of trichlorosilane acting as solvent was estimated by cooling one solution to −78.6° and removing the trichlorosilane volatile at that temperature. The remaining solid was warmed to 0° where the observed equilibrium dissociation pressure of trichlorosilane above it was 93 ± 1 mm. Trichlorosilane volatile at 0° was removed and determined to be 1.12 mmoles. Therefore, it was assumed that in all of these solutions there were 1.1 mmoles of solvation since the dissociation pressure of the trichlorosilane complex was well below the activity of trichlorosilane in each of the solutions examined.

(4) While the dissolved species presumably is $Si_6Cl_{14}·SiHCl_3$, the apparent molecular weight calculated here is based on a weighed amount of unsolvated material. If the solvation correction described in footnote (3) is not applied to the mmoles of available solvent, the apparent molecular weight is calculated to be 688 ± 8.

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PREPARATION OF 2-THIOURIDINE 5′-DIPHOSPHATE AND THE ENZYMATIC SYNTHESIS OF POLYTHIOURIDYLIC ACID

Sir:

In order to gain further insight into the biological role of polynucleotide phosphorylase,[1] we have initiated experiments designed to test the nucleoside diphosphates of several purine and pyrimidine analogs as substrates for this enzyme. 2-Thiouracil is incorporated into ribonucleic acid (RNA) of tobacco mosaic virus[2] and *Bacillus megatherium*,[3] *in vivo*. If polynucleotide phosphorylase is involved in RNA biosynthesis, then 2-thiouridine 5′-diphosphate should serve as a substrate for the enzyme, *in vitro*. This communication describes the preparation of three new thiouridine derivatives (2-thiouridine 5′-phosphate, 2-thiouridine 5′-phosphoramidate and 2-thiouridine 5′-diphosphate) and the utilization of thiouridine diphosphate for the enzymatic synthesis of polythiouridylic acid, *in vitro*.

2′,3′-Isopropylidene 2-thiouridine (I) was prepared from uridine by the five step synthesis of Brown, *et al.*[4] The protected nucleoside (I, 3 mmoles) was phosphorylated with β-cyanoethylphosphate (8.2 mmoles) and dicyclohexylcarbodiimide (24 mmoles) in dry pyridine.[5] The β-cyanoethyl ester of 2′,3′-isopropylidene 2-thiouridine 5′-phosphate (II) was treated with dilute alkali and then with acid to remove the blocking

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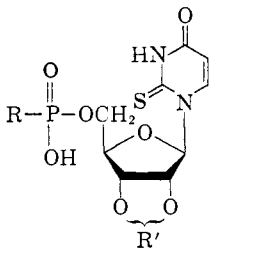

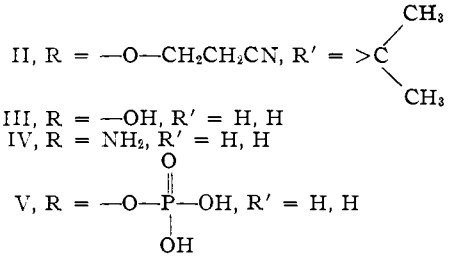

groups. 2-Thiouridine 5′-phosphate (III) was isolated in 56% yield based on I. Thiouridylic acid was converted to the N,N′-dicyclohexylguanidinium salt of 2-thiouridine 5′-phosphoramidate (IV) using the conditions described previously for uridine 5′-phosphoramidate,[6] but substituting dimethylformamide for formamide in the solvent mixture (83% yield). The amidate (IV, 0.45 mmole) was converted to 2-thiouridine 5′-diphosphate (V, TUDP) using dioxane diphosphoric acid[7] as described previously.[8] The product was isolated by ion exchange chromatography on Dowex-1-chloride (1.4 × 7 cm., 8% cross-linked): 0.003 *N* HCl + 0.04 *M* LiCl, 508 ml., TOD^{275} [9] = 595; 0.003 *N* HCl + 0.1 *M* LiCl, two peaks, 234 ml., TOD^{275} = 102; 590 ml., TOD^{275} = 3,780 (TUDP).

The isolated lithium salt[10] (100 mg., 42% yield based on IV) was slightly yellow. It gave a single ultraviolet absorbing spot upon electrophoresis (*p*H 3.5, citrate buffer) and it was recovered quantitatively from a single symmetrical peak after rechromatography by ion exchange.[11] Its ultraviolet absorption spectra at *p*H 2, 7 and 9 were similar to that of 2-thiouridine.[12]

Anal. S:labile P:total P: 1.06:1.00:2.00. Theoretical: 1.00:1.00:2.00.

In the presence of polynucleotide phosphorylase, TUDP showed an activity similar to UDP in the P^{32} exchange assay.[13] Polythiouridylic acid was synthesized by incubating TUDP (21 μmoles) with polynucleotide phosphorylase (4 units, gel fraction[13]) in 0.4 ml. of *p*H 8.0 Tris buffer (60 μmoles) containing Versene (0.4 μmole) and magnesium chloride (2 μmoles) at 30° for 4 hours.[14] The product was isolated as a white solid.[15] The polymeric nature of this material is indicated by gel formation during synthesis and its high sedimentation coefficient, S_{20} = 43 (cacodylate buffer *p*H 7, μ = 0.2), in the ultracentrifuge.

These results suggest that polynucleotide phosphorylase may be involved in the incorporation of 2-thiouracil into RNA *in vivo*. Further experiments on the preparation of mixed polynucleotides containing thiouridylic acid as well as the naturally occurring nucleotides are in progress.

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(9) TOD^{275} = optical density (1 cm. light path) × volume (ml.) at 275 mμ and *p*H = 2.7.

(10) Isolation as described in ref. 8.

(11) UDP and TUDP are well separated by ion exchange. No contamination of the product with UDP could be detected.

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(14) Release of inorganic phosphate corresponded to 55% of the labile phosphate in TUDP.

(15) The isolation procedure was similar to that described previously for other polynucleotides; see ref. 13.

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REDUCTIVE DEAMINATION OF ALIPHATIC AMINES

Sir:

A direct method for effecting reductive deamination of aliphatic primary amines ($RNH_2 \rightarrow RH$) has not been available.[1] We now have found that this conversion can be brought about if a sulfonamide derivative of the amine in alkaline medium is treated with hydroxylamine-O-sulfonic acid ($^+NH_3OSO_3^-$).[2] This general procedure was used: the sulfonamide (1 g.) was dissolved in a hot alkaline solution (*ca.* 100 ml.) made up from sodium hydroxide (10–12 g.), water (70–90 ml.) and ethanol[3] (10–30 ml.). Solid $^+NH_3OSO_3^-$ (15–25 equivalents[4]) was added in small batches (*ca.* 0.5 g. every minute).[5] The mixture was distilled (*ca.* 1 hr.) and the product (hydrocarbon) was extracted from the aqueous distillate with CCl_4 and assayed by infrared spectroscopy. Unconverted sulfonamide was recovered from the original mixture by acidification, then extraction.

The generality of the reaction is indicated by our results (Table I) with a variety of aliphatic amines (and even with an aromatic amine). The yields vary widely but are generally excellent when corrected for recovered starting material. Clearly, optimum conditions for conversion have not been defined, and many modifications (even in the nature of the reagent itself) suggest themselves.

A reasonable pathway for the reaction is shown. The formation of the N–N bond is of added attraction because it might involve an electron deficient

(1) In contrast, this transformation is accomplished easily in the aromatic series (N. Kornblum, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. II, 1944, p. 262).

(2) F. Sommer, O. Schulz and M. Nassau, *Z. anorg. allgem. Chem.*, **147**, 142 (1925).

(3) Sometimes ethanol could be omitted, but usually it was needed to help keep the sulfonamide dissolved.

(4) The reagent decomposes in aqueous alkali[2] and in ethanol (R. Nast, K. Nyul and E. Grziwok, *ibid.*, **267**, 304 (1952)).

(5) This allowed sufficient time for boiling and gas evolution to subside between additions.