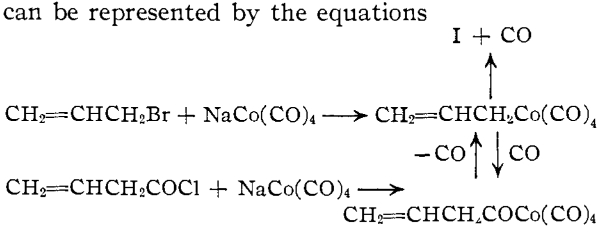
evolved slowly on standing and the spectrum changes to that of I; "crotyl bromide" reacts analogously. That an unstable acylcobalt tetracarbonyl is formed initially in these reactions has been shown by treating $NaCo(CO)_4$ with vinylacetyl chloride at 0°. The initial reaction mixture shows the 5.8 μ band, but on standing about 2 moles of carbon monoxide is evolved and distillation yields pure I. The course of the reaction can be represented by the equations



$$\begin{tikzcd} & I + CO \\ CH_2{=}CHCH_2Br + NaCo(CO)_4 \arrow[r] & CH_2{=}CHCH_2Co(CO)_4 \arrow[u] \arrow[d, shift left, "CO"] \\ CH_2{=}CHCH_2COCl + NaCo(CO)_4 \arrow[r] & CH_2{=}CHCH_2COCo(CO)_4 \arrow[u, shift left, "-CO"] \end{tikzcd}$$

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KINETICS OF THE METAL-AMMONIA-ALCOHOL REDUCTION OF BENZENE

Sir:

In a recent paper[1] we reported (1) that the reduction of benzene with stoichiometric quantities of lithium and ethanol followed over all third-order kinetics, and (2) that the individual orders with respect to alcohol and lithium in the lithium-ammonia-*t*-butyl alcohol reduction of benzene were unity, as determined by the method of initial rates. We concluded[2] that the rate law governing this type of reaction is

$$-d(ArH)/dt = k(ArH)(M)(ROH) \qquad (1)$$

Our evidence has been criticized by Eastham, Keenan and Secor[3] on the grounds that competing hydrogen evolution would invalidate the kinetic analysis in the first of the above studies. However, our preliminary experiments[1] indicated a high yield (94%) of dihydrobenzene from the lithium-ethanol reduction so that the slight downward deviation expected in the third-order plot (visible in our published data) would be insufficient to obscure the third-order adherence.[4]

TABLE I

INITIAL REDUCTION RATES OF BENZENE WITH LITHIUM AND *t*-BUTYL ALCOHOL IN LIQUID AMMONIA-6% ETHYL ETHER

Run	$[C_6H_6]$	[Li]	[*t*-BuOH]	Time in sec.	Moles of dihydrobenzene produced
1[a]	[0.062]	[0.124]	[0.124]	50	0.0023
				100	0.0038
2[a]	[0.124]	[0.124]	[0.124]	50	0.0043
				100	0.0077
3[a]	[0.062]	[0.248]	[0.124]	50	0.0044
				100	0.0080
4[a]	[0.062]	[0.124]	[0.248]	50	0.0046
				100	0.0079

[a] Data quoted under Runs 1 and 2 are averages of duplicate runs. Runs 3 and 4 are single runs; however, *cf.* Table III, reference 1.

We have nevertheless redetermined the orders with respect to the three reactants benzene, lithium, and *t*-butyl alcohol, by the method of initial rates,[5] a method insensitive to the presence of minor side reactions. Experimental techniques were as previously reported.[1]

Our data are presented in Table I. It is observed that doubling the concentration of each reactant doubles the initial reduction rate within experimental error. Therefore, the concentration of each reactant enters the rate law in the first power. Our conclusions based on the previous study are thereby confirmed.

In our study of the effect of proton source, nature of metal, and added salts,[1] the rate constants for the slow reductions with sodium and potassium were calculated from the slopes of third-order plots covering a small fraction of reaction. In these cases, hydrogen evolution can compete more effectively,[2] and the quoted rate constants are probably low by 20-30% for the sodium reductions and by a factor of 2-3 for the potassium reduction.

Our conclusions with respect to mechanism are unaffected by these differences.

Acknowledgment.—We wish to thank Professors J. F. Eastham and C. W. Keenan for making copies of their manuscript available to us before publication.

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[1] A. P. Krapcho and A. A. Bothner-By, THIS JOURNAL, **81**, 3658 (1959).

[2] The conclusion rested on the basis of the two cited pieces of evidence. No conclusions concerning the form of the kinetic law were drawn from data on reductions with sodium or potassium. These runs were made for the purpose of comparing rates of reduction with different alkali metals, and are discussed in a separate section of our paper.

[3] J. F. Eastham, C. W. Keenan and H. V. Secor, THIS JOURNAL, **81**, 6523 (1959).

[4] We are unable to account for the discrepancy between our findings and that reported by Eastham, *et al.*,[3] who, for lithium reduction, found 12% hydrogen evolution at a time when only 60% of the benzene was reduced. We have repeated their measurements of hydrogen evolution during the sodium-ammonia-ethanol reduction of benzene, using vacuum line techniques in order to reduce initial concentrations of water, oxygen, peroxides, or other catalytic species, and have found 15% hydrogen evolution after 2700 sec. It is not clear, however, whether this lower value reflects lower initial rates of hydrogen evolution, or merely a subsequent deceleration, as noted in an earlier paper (J. F. Eastham and D. R. Larkin, *ibid.*, **81**, 3652 (1959)).

[5] R. Livingston, in "Techniques of Organic Chemistry," Vol. VIII, Interscience Publishers, New York, N. Y., 1953, p. 183 ff.

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A NEW SYNTHESIS FOR HEXASILICON TETRADECACHLORIDE,[1] Si_6Cl_{14}

Sir:

In the presence of trimethylamine,[2] disilicon hexachloride, Si_2Cl_6, undergoes a quantitative

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[1] The authors gratefully acknowledge the partial support of this project by a Research Corporation Frederick Gardner Cottrell Grant. This work was presented in part at the 133rd meeting of the American Chemical Society.

[2] With pure Si_2Cl_6 at room temperature a small trace of amine is sufficient. The disproportionation is inhibited by $TiCl_4$ and O_2. These inhibitions can be overcome by the use of larger amounts of amine. In this case, however, the resulting Si_6Cl_{14} is contaminated with titanium complexes or chlorosiloxanes and the net yield is diminished by losses during purification, effected by sublimation *in vacuo* at 125° or by recrystallization from trichlorosilane or diethyl ether solutions

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

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 $\mathrm{SiCl_4}$. 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 $\mathrm{SiCl_4}$.

The white microcrystalline solid remaining in the tube had the composition $(\mathrm{Si_{1.00}Cl_{2.36}})_x$, 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

	$\mathrm{SiHCl_3}$				
° 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 $\mathrm{Si_6Cl_{14}}$, 664.8.

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

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

Traces of trimethylamine catalyze further disproportionation of $\mathrm{Si_6Cl_{14}}$ at elevated temperatures to $\mathrm{SiCl_4}$ and a yellow solid, $(\mathrm{Si_{1.00}Cl_{1.80}})_x$, 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.

$\mathrm{Si_6Cl_{14}}$ 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.

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

Differences in properties between the $\mathrm{Si_6Cl_{14}}$ 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 $\mathrm{Si_6Cl_{14}}$.

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(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 $\mathrm{Si_6Cl_{14}{\cdot}SiHCl_3}$, 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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(1) M. Grundberg-Manago and S. Ochoa, THIS JOURNAL, **77**, 3165 (1955).

(2) R. Jeener and J. Rosseels, *Biochim. Biophys. Acta*, **11**, 438 (1953).

(3) R. Hamers, *ibid.*, **21**, 170 (1956).

(4) D. M. Brown, D. B. Parihar, A. Todd and S. Varadarajan, *J. Chem. Soc.*, 3028 (1958).

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