

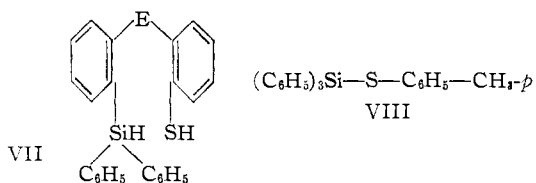
manner to give 10,10-diphenylphenazasiline² (II) in a 1.2% yield, m.p. 197–198°; *Anal.* Calcd. for C₂₄H₁₉NSi: C, 82.49; H, 5.48; Si, 8.03. Found: C, 82.08, 82.27; H, 5.28, 5.23; Si, 8.10. On metalation of II with *n*-butyllithium, followed by treatment with ethyl sulfate, 5-ethyl-10,10-diphenylphenazasiline (III) was formed in an almost quantitative yield, m.p. 122–123°. *Anal.* Calcd. for C₂₆H₂₃NSi: C, 82.74; H, 6.14; N, 3.71; Si, 7.41. Found: C, 82.35; H, 6.03; N, 4.39, 4.12; Si, 7.48. The same compound III was obtained in a 6.6% yield from the reaction of diphenylsilane with 10-ethylphenothiazine after heating for 6 days at reflux temperature.

From the reaction of diphenylsilane and thianthrene (1:1 ratio), after heating for 3.5 days at 250–260° and working up in the manner described above, 10,10-diphenylphenothiasilin² (IV) was obtained in a 4.7% yield, m.p. 157–158°. *Anal.* Calcd. for C₂₄H₁₉SSi: Si, 7.66. Found: Si, 7.72. The compound was oxidized with hydrogen peroxide in acetic acid to form 10,10-diphenylphenothiasilin-5-dioxide (V), m.p. 208–209°, which was shown to be identical with an authentic sample obtained from the reaction of 2,2'-dilithiodiphenyl sulfone and diphenyldichlorosilane.³ An attempt to isolate 5,5,10,10-tetraphenylsilanthrene² (VI) from the reaction of diphenylsilane and thianthrene in a 2:1 ratio has so far been unsuccessful; only 4.05% of IV was obtained. Thianthrene-5-dioxide⁴ also evolved hydrogen sulfide on heating with diphenylsilane, but attempts to isolate V from the reaction mixture were unsuccessful.

Whereas in all reactions essentially no diphenylsilane was recovered, the sulfur heterocycle was recovered in yields ranging from 20 to 50%. Triphenylsilane⁵ was obtained in 5–16% yields as a by-product in all reactions, together with traces of tetraphenylsilane.⁵

Since hydrogen sulfide was evolved on exposure of the crude reaction mixtures to moisture and on chromatography of the distillation fractions on alumina, the formation of Si-S-H or Si-S-Si type by-products is postulated. Such products might have resulted as a consequence of reaction between hydrogen sulfide and diphenylsilane or triphenylsilane.

In order to throw light on the possible intermediate formation of a triphenylsilane-thiophenol type VII, which in a further step splits off hydrogen sulfide to form the silicon heterocycle



the reaction between triphenylsilane and *p*-thiocresol was investigated. On heating an equi-

(2) The names and the numbering systems used herein were recommended by the editorial staff of *Chemical Abstracts*.

(3) K. Oita and H. Gilman, *J. Org. Chem.*, **22**, 336 (1957).

(4) H. Gilman and D. R. Swayampati, *THIS JOURNAL*, **77**, 5946 (1955).

(5) These compounds may have been formed by disproportionation of diphenylsilane. See H. Gilman and D. Miles, *ibid.*, in press.

molecular mixture for 5 days at 220–230°, however, none of the expected triphenyl-*p*-tolylsilane was formed, but triphenyl-*p*-thiocresoxysilane (VIII) was obtained in a 69% yield, m.p. 79–80°. *Anal.* Calcd. for C₂₅H₂₂SSi: Si, 7.33. Found: Si, 7.27. The structure of VIII was established by hydrolysis with alkali, which gave *p*-thiocresol, triphenylsilanol and hexaphenyldisiloxane. From the reaction of VIII with triphenylsilyllithium in tetrahydrofuran, hexaphenyldisilane was isolated in an 82% yield and *p*-thiocresol in a 57% yield.

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BIOSYNTHESIS OF GLYCOGEN FROM URIDINE DIPHOSPHATE GLUCOSE¹

Sir:

Previous work has shown that UDPG² acts as glucose donor in the synthesis of trehalose phosphate,³ sucrose,⁴ sucrose phosphate⁵ and cellulose.⁶

TABLE I
ANALYTICAL CHANGES

The complete system contained: 0.5 μmole of UDPG, 0.33 μmole of glycogen, tris-(hydroxymethyl)-amino-methane buffer of pH 7.4, 0.01 M ethylenediaminetetraacetate and 0.02 ml. of enzyme. Total volume 0.07 ml. Incubation: 45 min. at 37°. The enzyme was prepared from an aqueous extract of rat liver by acidification to pH 5. The precipitate was washed four times with acetate buffer of pH 5 and redissolved in buffer. Results in μmoles.

	ΔUDPG ^a	Δ Glycogen ^b
Complete system	0.22	0.27
No UDPG	0	-0.03

^a Estimated with pyruvate kinase.⁷ ^b Measured with a phenol-sulfuric acid reagent after precipitation with ethanol⁸ and expressed as glucose.

When UDPG is incubated with a liver enzyme and a small amount of glycogen the chemical changes shown in Table I were found to take place. Approximately equal amounts of UDP and of glycogen were formed. Such an increase in glycogen could only be detected with liver preparations freed from amylase. Other preparations obtained

(1) This investigation was supported in part by a research grant (No. G-3442) from the National Institutes of Health, U. S. Public Health Service, and from Laboratorios de Investigación de E. R. Squibb & Sons Argentina, S. A.

(2) UDPG = uridine diphosphate glucose; UDP = uridine diphosphate.

(3) L. F. Leloir and E. Cabib, *THIS JOURNAL*, **75**, 5445 (1953).

(4) L. F. Leloir and C. E. Cardini, *ibid.*, **75**, 6084 (1953).

(5) L. F. Leloir and C. E. Cardini, *J. Biol. Chem.*, **214**, 157 (1955).

(6) L. Glaser, *Biochim. et Biophys. Acta*, **25**, 436 (1957).

(7) E. Cabib and L. F. Leloir, *J. Biol. Chem.*, in press.

(8) H. Montgomery, *Arch. Biochem. Biophys.*, **67**, 378 (1957).

by ammonium sulfate precipitation contained amylase and therefore lost their glycogen. With such enzymes no UDP formation took place unless a primer was added. As shown in Table II glycogen and soluble starch acted as primers whereas glucose and maltose were ineffective. Several mono-, di- and oligosaccharides and hexose phosphates were tested with negative results. Treatment of glycogen with α -amylase destroyed its priming capacity. It can be concluded that UDPG acts directly as a glucose donor to glycogen and that the reaction is thus similar to polysaccharide formation from glucose 1-phosphate with animal phosphorylase which requires a primer of high molecular weight. The enzyme was found in the soluble fraction of liver and became very unstable after purification.

TABLE II
PRIMER REQUIREMENT

System as in Table I, but glycogen omitted. The enzyme (0.01 ml.) was obtained by precipitation with 1.6 *M* ammonium sulfate followed by dialysis. Incubated 60 min. at 37°.

Additions	Δ UDP (μ moles)
None	0
0.1 mg. glucose	0
0.2 mg. maltose	0
0.4 mg. glycogen	0.08
0.4 mg. soluble starch	0.06

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DETONATION OF LIQUID OXYGEN-LIQUID METHANE SOLUTIONS

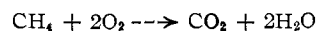
Sir:

The classical theory of detonation was developed from the study of simple explosive *gas* mixtures, such as: $H_2 + O_2$, $CO + O_2$, or $CH_4 + O_2$.

powder and liquid oxygen, liquid or solid ozone, lead to very simple detonation products. In many cases only *individual compounds* are formed (*i.e.*, $2 CO + O_2 \rightarrow$ only CO_2 , $O_3 \rightarrow$ only O_2 , $2 H_2 + O_2 \rightarrow$ only H_2O) in contrast to the usual condensed explosives like TNT, tetryl, PETN, nitroglycerine, etc., (*i.e.*, $TNT \rightarrow CO_2$, CO , $C_{sol.}$, H_2O , H_2 , N_2 and some CH_4). Thus an opportunity is provided to study, both experimentally and theoretically, *single compounds* or very simple mixtures in a region of temperatures and pressures far beyond the usual.

The preliminary detonation velocities shown in Table I were obtained with $CH_4(liq.)-O_2(liq.)$ mixtures, using the rotating mirror equipment of the Naval Ordnance Laboratory. The mixtures were prepared in Dewar flasks in quantities of ≈ 500 cc. by mixing desired amounts of liquid O_2 and CH_4 , and their detonation was initiated by an electric blasting cap and a plane wave booster with tetryl and RDX composition B.

The maximum detonation velocity for the *gas* systems is reached with the 1:1 molar mixture. The *liquid* maximum is close to the composition



This corresponds to the maximum energy release (see Table I) and could be anticipated since the high detonation pressure (calcd. $\approx 6.8 \times 10^4$ atm.), stabilizes both the CO_2 and H_2O molecules, which dissociate at the high temperature and low pressure of the gaseous system.

The theoretical values have been calculated using standard procedures¹ and are substantially higher than our experimental results. Small amounts (1-2%) of N_2 which conceivably may have dissolved in our mixtures, cannot account for this discrepancy.

Additional measurements with the simplest possible systems, *i.e.*, $(CO)_{liq.} + (O_2)_{liq.}$ and pure

TABLE I

Molar ratio $O_2:CH_4$	ΔE 90°K., kcal./mole	Liquid density at 90°K., g./cm. ³	Exptl. Detonation velocity, m./sec.		Calcd. values for liquid system		
			Gas at 300°K.	Liq. at 90°K.	Detonation velocity, m./sec.	Detonation temp., °K.	Detonation pressure $\times 10^{-4}$, atm.
4.00	173.10	0.980	2075 ^a	3325	4400	4150	8.1
2.00	180.18	.879	2322 ^b	5120	6010	5830	6.8
1.50	114.10	.830	2470 ^b	5110	5840	4670	5.0
1.00	57.85	.755	2528 ^b	4615	5250	3040	2.9

^a R. B. Morrison, Univ. of Michigan, Report UMM-97, Jan. 1952, p. 99. ^b B. Lewis and G. von Elbe, "Combustion, Flames and Explosion of Gases," Academic Press, Inc., New York, N. Y., 1951, p. 584. (H. B. Dixon's data 1894, 1903.)

The study of the same systems, in *liquid* or *solid* phase, has, however, not been undertaken to our knowledge. In connection with this Institute's high temperature research, it was found that liquid CO and CH_4 form clear homogeneous solutions with liquid O_2 over the whole composition range from 0 to 100% O_2 . They are colorless on the CH_4 - or CO -rich side and gradually approach the color of liquid O_2 on the O_2 -rich side. They detonate with great brisance.

These mixtures, as well as others, such as liquid hydrogen and solid oxygen powder, solid cyanogen

O_3 , as well as their theoretical study, are desirable to explain the above discrepancy.

The liquid system was found to detonate at least in the range from 11 to 67 mole % CH_4 , while the inflammability range of the gas system is 5.4 to 59.2 mole % CH_4 .

We wish to thank the Office of Ordnance Research for its financial support, and the Naval Ordnance Laboratory and their Dr. S. J. Jacobs

(1) J. Taylor, "Detonation in Condensed Explosives," The Clarendon Press, Oxford, England, 1952, pp. 87-110.