placed by succinate, in which case photoreduction of DPN proceeds several times faster than in the presence of $FMNH_2$; here again TPN cannot replace DPN.

TABLE I

RATES AND REQUIREMENTS OF LIGHT INDUCED OXIDATION-REDUCTION REACTIONS

(Rates in μmoles per hr. per μmole chlorophyll[a])

All preparations made up to 3.0 ml. in 0.1*M* glycylglycine (*p*H 7.5) (chlorophyll content of chromatophores from 0.02 to 0.025 μM.). Further additions as indicated: DPN, TPN 0.7 μM. DPNH, 0.1 μM. FMN, 0.15 μM. $FMNH_2$ (catalytically reduced with H_2), 0.05–0.15 μM. Samples degassed in anaerobic cuvettes.

		Light			Dark period following illumination		
	Additions	Subs. meas.	Reduced	Oxidized	Subs. meas.	Reduced	Oxidized
1	FMN	FMN	0.0				
2	$FMNH_2$	$FMNH_2$	...	0.3	$FMNH_2$	...	0.3
3	DPN + DPNH	DPNH	...	0.2	DPNH	...	0.2
4	DPN + $FMNH_2$	DPN	9.1	...	DPNH	...	0.6
		$FMNH_2$	...	9.5	FMN	0.6	...
5	4(+ DPNH + FMN formed in the light) heated 2 min. at 60°	DPNH	...	0.6	DPNH	...	0.6
		FMN	0.6	...	FMN	0.6	...
6	TPN + $FMNH_2$	TPN	0.0				
		$FMNH_2$	...	0.3	$FMNH_2$	...	0.3

[a] Concentration changes measured at 15–20° with a Beckman DU Spectrophotometer. Actual changes in optical density at 340 mμ of the order of 0.1 ± 0.005 unit for an initial 10 min. period of illumination (initial o.d. 0.5–0.8); dark values of the order of 0.01 ± 0.002 unit per hour. FMN measured at 455 mμ. Difference spectra kindly measured by Dr. V. Lorber.

The purified chromatophores, without any added enzymes, can carry out either photophosphorylation[5] or photoreduction of DPN or both reactions simultaneously; photoreduction of DPN is partially inhibited when photophosphorylation occurs at the same time.

Vernon[6] has described a system from *R. rubrum*, fortified with a number of enzymes, which preferentially photoreduces TPN (as indicated by suitable trapping agents); it is hoped that the basis for this difference in pyridine nucleotide specificity can be ascertained soon.

The pyridine nucleotide specificity and the high lability of the system make it plausible that one is dealing with an enzymatic reaction and not simply with a non-enzymatic, chlorophyll sensitized reaction.[7] Thus, the simultaneous stoichiometric reduction of DPN and oxidation of $FMNH_2$ in the light represent a reaction in bacterial preparations analogous to the Hill reaction of illuminated chloroplasts[1,2] (*cf.* 8).

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RECEIVED MAY 8, 1958

(6) L. P. Vernon, THIS JOURNAL, **80**, 246 (1958); *Federation Proc.*, **17**, 328 (1958).

(7) A. A. Krasnovskii and G. P. Brin, *Compt. Rend. (Doklady) Acad. Sci. U.S.S.R.*, **67**, 325 (1949).

(8) L. P. Vernon and M. D. Kamen, *Arch. Biochem. Biophys.*, **51**, 122 (1954).

THE REACTION OF PHOSPHINE METHYLENES WITH BORON HYDRIDES

Sir:

Triphenylphosphine methylene (I, $(C_6H_5)_3P^+CH_2^-$) may be regarded as a carbanion stabilized by π-bonding of the unshared pair with adjacent phosphorus orbitals. It therefore appeared probable that this material would interact with electron-deficient boron hydrides such as diborane and decaborane to produce compounds containing P–C–B bonding.

Diborane Reactions.—Addition of gaseous diborane to an ethereal solution of I in diethyl ether at room temperature resulted in rapid decolorization and the deposition of triphenylphosphine methylene boron trihydride (II, $(C_6H_5)_3P^+CH_2BH_3^-$). The product, II, proved to be stable toward water and was recrystallized easily from methylene chloride–diethyl ether solution. Hydrolysis with aqueous hydrobromic or hydrochloric acids afforded three moles of hydrogen per mole of boron trihydride and the corresponding triphenylmethylphosphonium halide.

$$C_6H_{33}P^+CH_2BH_3^- + 4HX \xrightarrow{H_2O} (C_6H_5)_3P^+CH_3X^- + 3H_2 + BX_3$$

Iodine was reduced to iodide ion and silver ion was reduced to silver metal by II in alcoholic solution.

Table I presents the preparation data and properties of II and two other triphenylphosphine methylene boron trihydrides which have substituents on the methylene carbon. Each of these compounds displayed strong B–H stretching bands at 4.40 and 4.50μ.

TABLE I

PREPARATION AND PROPERTIES OF TRIPHENYLPHOSPHINE-METHYLENE BORON TRIHYDRIDES

R in $(C_6H_5)_3P^+CHRBH_3$	M.p., °C.	% Yield from $(C_6H_5)_3P^+CH_2RBr$	Moles H_2 Mole Compd.
H	191–192°	45	3.02
CH_3	171–172°	38	2.98
C_6H_5	143–144°	42	2.90

	Calculated, %			Found, %		
	C	H	B	C	H	B
H	78.65	6.95	3.72	78.40	7.16	3.50
CH_3	78.97	7.29	3.56	78.80	7.21	3.71
C_6H_5	81.98	6.61	2.95	81.62	6.68	3.18

The formation of II from I and diborane is in sharp contrast to the results of Wiberg and Strebel[1] who reported the reaction of ethylmagnesium halides and diborane to produce triethylborane and magnesium halohydrides, HMgX.

Decaborane Reactions.—The addition of an ethereal solution of decaborane[2] to a similar solution of I produced an oil which crystallized on standing to give a 35% yield of bright yellow rhombs (III). The product was recrystallized easily from methylene chloride–diethyl ether, m.p. 127–129°; $C_{19}H_{31}B_{10}P$ (found: C, 56.8; H, 8.01; B, 25.9; P, 7.60. Calculated: C, 57.25; H, 7.84; B, 27.14; P, 7.77). The infrared spectrum of III contained B–H stretching at 4.05μ (terminal) and

(1) E. Wiberg and P. Strebel, *Ann.*, **607**, 9 (1957).

(2) Obtained from American Potash and Chemical Co., Henderson, Nevada.

5.30μ (bridge) as well as the bands commonly associated with the triphenylmethyl phosphonium ion. Acidification of III with dilute hydrochloric acid produced immediate decolorization and decaborane was recovered in 50% yield. Air oxidation and hydrolysis of III was not apparent after three months at ambient temperature.

It appears that this material is the triphenylmethylphosphonium salt of decaborane and is the first such material to be isolated as a pure stable

$$(C_6H_5)_3P^+CH_2^- + B_{10}H_{14} \longrightarrow (C_6H_5)_3P^+CH_3B_{10}H_{13}^-$$

substance.

The reactions of other phosphine methylenes with decaborane are under investigation.

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RECEIVED MAY 23, 1958

ISOLATION OF GUANOSINE DIPHOSPHATE FUCOSE FROM AEROBACTER AEROGENES

Sir:

We wish to report the isolation of a new sugar nucleotide, guanosine diphosphate fucose, from a strain of Aerobacter aerogenes[1] that produces a polysaccharide containing L-fucose.[2]

The nucleotides from 150 g. wet weight of bacteria were extracted with boiling 70% ethanol, precipitated with mercuric ion, and chromatographed on a Dowex 1-Cl$^-$ column.[3] Elution with 0.01 *N* HCl and increasing concentrations of NaCl yielded an ultraviolet absorbing peak which was determined to be 75% uridine diphosphate glucose and uridine diphosphate galactose by enzymatic analysis.[4] This peak contained a total of 10 μM. of nucleotides calculated as uridine from spectral data. A minor component of this fraction amounting to 10% of its optical density at 260 mμ could be isolated by paper electrophoresis or paper chromatography. The ultraviolet absorption spectrum of this component was typical of a guanosine derivative. Its mobility during electrophoresis in sodium formate buffer, *p*H 3.5, was less than guanosine diphosphate, but greater than guanosine monophosphate while it had a higher R_f than guanosine monophosphate when chromatographed with ethanol-neutral ammonium acetate solution.[5]

The isolated component was analyzed colorimetrically[6] and found to contain approximately 0.8 μM. of 6-deoxyhexose per μM. guanosine. The absorption peak at 400 mμ given by the guanosine derivative in this test was identical in shape with that given by authentic fucose and also disappeared at the same rate upon dilution with water.[7]

Hydrolysis of the guanosine derivative in 0.01 *N* HCl at 100° for 10 minutes liberated a compound having an R_f identical with that of fucose when chromatographed with butanol–acetic acid–water,[8] phenol–water,[8] or pyridine–ethyl acetate–water.[9] In addition, an ultraviolet absorbing compound was formed which exhibited the same chromatographic and spectral properties as guanosine diphosphate. Longer hydrolysis led to the formation of a second ultraviolet absorbing compound which exhibited the same properties as guanosine monophosphate.

In view of the well-established role of the uridine sugar nucleotides as glycosyl donors in the biosynthesis of many complex saccharides, it is an interesting variation to find fucose occurring in a guanosine nucleotide. The only other guanosine sugar nucleotide known at present is guanosine diphosphate mannose.[10,11]

(1) Strain A_8S_1 (ATCC 12657).
(2) J. F. Wilkinson, W. F. Dudman and G. O. Aspinall, *Biochem. J.*, **59**, 446 (1955).
(3) E. Cabib, L. F. Leloir and C. E. Cardini, *J. Biol. Chem.*, **203**, 1055 (1953).
(4) H. M. Kalckar, E. P. Anderson, and K. J. Isselbacher, *Biochim. Biophys. Acta*, **20**, 262 (1956).
(5) A. C. Paladini and L. F. Leloir, *Biochem. J.*, **51**, 426 (1952).
(6) Z. Dische and L. B. Shettles, *J. Biol. Chem.*, **175**, 595 (1948).
(7) Z. Dische and L. B. Shettles, *ibid.*, **192**, 579 (1951).
(8) S. M. Partridge, *Biochem. J.*, **42**, 238 (1948).
(9) M. A. Jermyn and F. A. Isherwood, *ibid.*, **44**, 402 (1949).
(10) E. Cabib and L. F. Leloir, *J. Biol. Chem.*, **206**, 779 (1954).
(11) J. L. Strominger, *Biochim. et Biophys. Acta*, **17**, 283 (1955).
(12) U. S. Public Health Service Postdoctoral Fellow.

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RECEIVED APRIL 5, 1958

ORGANOBORON COMPOUNDS. X. MIXED TRIALKYLBORANES DISTILLABLE WITHOUT DISPROPORTIONATION[1,2]

Sir:

It was suggested recently[1] that mixed trialkylboranes characterized by the presence of a *t*-butyl group may manifest unusual stability to disproportionation. One such substance, diisobutyl-*t*-butylborane, was described previously and its stability to disproportionation was attributed to steric interference with the disproportionation mechanism.[1]

We wish to describe now the first distillable trialkylborane containing *three dissimilar alkyl groups*, namely, *t*-butyl-isobutyl-*n*-amylborane. This substance, b.p. 43.5–44.0° at 0.5 mm., $n^{25}D$ 1.4296, d^{25} 0.7506, was fractionally distilled twice *in vacuo* without decomposition, rearrangement or disproportionation. *Anal.* Calcd. for $C_{13}H_{29}B$: B, 5.52. Found: B, 5.56. MR_D: calcd.,[3] 67.30; obsd., 67.48. Oxidation with alkaline hydrogen peroxide[1] produced equimolar quantities of *t*-butyl, isobutyl and *n*-amyl alcohols in high yield.

t-Butyl-isobutyl-*n*-amylborane was prepared in two ways: (a) in 50% yield by the alkylation of *n*-amyldifluoroborane with *t*-butylmagnesium chloride in anhydrous ether; (b) in 30% yield by the reaction of *t*-butyl-di-*n*-amylborane with isobutylmagnesium bromide.[4] The physical constants and the infrared spectra of the two samples were practically identical. In connection with method (a), it is noteworthy that one *t*-butyl group derived from the Grignard reagent rearranges to isobutyl during the alkylation reaction. Concerning

(1) Previous paper, G. F. Hennion, P. A. McCusker and A. J. Rutkowski, THIS JOURNAL, **80**, 617 (1958).
(2) Contribution from the Radiation Project operated by the University of Notre Dame and supported in part under Atomic Energy Commission Contract AT-(11)-38.
(3) The B–C bond refraction was taken as 1.93.
(4) S. L. Clark and J. R. Jones, Abstracts, 133rd Meeting, American Chemical Society, San Francisco, April, 1958, p. 34-L.