analog of the substitution reactions at the saturated carbon atom in the β-branched alkyl series (Et, Pr, *i*-Bu and neopentyl) where the decrease in rate along the series invariably is attributed to a steric effect. In the latter series the relative rates of substitution (bromide for isotopic bromide) are[6]: 100, 65, 3.3 and 0.0015.

The comparison between the two series provides striking evidence of the similarity of the geometrical arrangement of the transition states for substitution at carbon and at sulfur. Just as in the carbon analog, it is seen easily that steric hindrance, and the consequent drop in reactivity, is justified only if the entering group attacks the central atom from the back side. If attack were possible from other directions, either making an angle of 90° or 120°, no such decrease could be justified. It must then be concluded that the linear arrangement is quite strongly favored. It may be observed that this arrangement is also the most favorable from the viewpoint of electrostatics. However, elementary considerations show that electrostatics alone would provide but a minor contribution to the total free energy difference between the various arrangements.

(6) P. D. B. de la Mare, *J. Chem. Soc.*, 3180 (1955).

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EUROPIUM HEXABORIDE AND LANTHANUM TETRABORIDE[1]

Sir:

It is well known[2] that the effective atomic radii of the rare earth elements decrease regularly with increasing atomic number, with the exceptions of Eu and Yb.

In a recent paper[3] it was pointed out that the lattice constants of the cubic rare earth hexaborides also decrease with increasing atomic number of the metal atoms, with the significant exception of YbB_6. No data for europium borides were then available. It was also noted that the rare earth tetraborides showed no such anomalies; the lattice constants of these compounds, including YbB_4, decrease monotonically with increasing atomic number of the metal atom.

Recently a quantity of Eu_2O_3 of high purity was made available to us and efforts were made to prepare EuB_6 and EuB_4. The former was readily prepared by heating the metal oxide with the appropriate amount of boron; B_2O_3 was evolved and the hexaboride remained in the reaction chamber. Reaction products were studied primarily by X-ray diffraction methods. The compound exhibited a considerable range of homogeneity; the lattice constant ranged from 4.170Å. for preparations somewhat deficient in boron, to 4.184Å. for preparations containing excess boron. The lattice constant of apparently stoichiometric preparations was 4.178Å. It is clear that the size anomaly observed by Klemm and Bommer in the rare earth elements is duplicated in the hexaborides.

Efforts also were made to prepare EuB_4, but, although preparative conditions (including reaction temperatures and specimen compositions) were varied over wide ranges, these were uniformly unsuccessful. When reaction occurred, the product invariably contained large amounts of EuB_6 with no signs of a tetraboride.

It appeared likely that the failure to prepare EuB_4 is related to the large effective size of the metal atom. As a check on this hypothesis, efforts were made to prepare LaB_4. After a number of failures, it was found possible to prepare LaB_4 of a satisfactory purity by reaction of lanthanum metal with boron in vacuum at about 1300°. The LaB_4 phase, like EuB_6, appears to have a wide range of homogeneity. Compositions containing from two to four parts of boron per metal atom yielded products containing the LaB_4 phase as a major component. When the boron content was less than that corresponding to "LaB_2," or when lanthanum oxide was used as a starting material, no LaB_4 was formed.

Lattice dimensions of LaB_4 did not appear to vary significantly with composition. The unit cell is tetragonal with $a = 7.30$ Å. and $c = 4.17$Å. It is isomorphous with CeB_4 and other rare earth tetraborides.[3]

It appears in view of our experience with LaB_4, that it may be possible to prepare EuB_4 by direct reaction of boron with metal; the latter, unfortunately, is not presently available to us.

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[1] Study supported by the Office of Naval Research.

[2] W. Klemm and H. Bommer, *Z. anorg. Chem.*, **231**, 138 (1937).

[3] B. Post, D. Moskowitz and F. W. Glaser, THIS JOURNAL, **78**, 1800 (1956).

SIMULTANEOUS REDUCTION OF DIPHOSPHOPYRIDINE NUCLEOTIDE AND OXIDATION OF REDUCED FLAVIN MONONUCLEOTIDE BY ILLUMINATED BACTERIAL CHROMATOPHORES[1]

Sir:

The direct spectroscopic observation of light induced reduction of pyridine nucleotides by chloroplasts has been described.[2,3] A similar reduction of DPN[4] can be observed with chromatophores from *Rhodospirillum rubrum* under highly anaerobic conditions on illumination with red light. Purified chromatophores[5] were used in this study to minimize dark reduction of DPN or TPN which may occur in crude preparations. It can be seen from Table I, 4, that in the reaction system described there is a close molar equivalence of DPN reduced and of $FMNH_2$ oxidized; furthermore, this equivalence holds for the much slower reverse reaction in the dark. $FMNH_2$ also can be re-

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[1] This investigation was supported by the Graduate School of the University of Minnesota and by the National Science Foundation (Grant G-1922).

[2] A. San Pietro and H. M. Lang, *Science*, **124**, 118 (1956); *J. Biol. Chem.*, **231**, 211 (1958).

[3] D. I. Arnon, F. R. Whatley and M. B. Allen, *Nature*, **180**, 182 (1957); *Science*, **127**, 1026 (1958).

[4] Abbreviations used: DPN, DPNH, respectively, for oxidized and reduced diphosphopyridine nucleotide; TPN for oxidized triphosphopyridine nucleotide; FMN, $FMNH_2$, respectively, for oxidized and reduced flavin mononucleotide.

[5] A. W. Frenkel, *J. Biol. Chem.*, **222**, 823 (1956).

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 +	DPN	9.1	...	DPNH	...	0.6
$FMNH_2$	$FMNH_2$	...	9.5	FMN	0.6	...
5 4(+ DPNH	DPNH	...	0.6	DPNH	...	0.6
+ FMN formed in the light) heated 2 min. at 60°	FMN	0.6	...	FMN	0.6	...
6 TPN +	TPN	0.0				
$FMNH_2$	$FMNH_2$	...	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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[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.

$$C_6H_{53}P^+CH_2BH_3^- + 4HX \xrightarrow{H_2O} (C_6H_5)_3P^+CH_3X^- + 3H_2 + BX_3$$

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 $(C_6H_5)_3$-P^+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

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

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