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).

DEPARTMENTS OF GENERAL AND OF ORGANIC CHEMISTRY, AND CENTER OF NUCLEAR CHEMISTRY
UNIVERSITY OF PADUA, ITALY
ANTONINO FAVA
ANTONIO ILICETO

RECEIVED MAY 16, 1958

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.

DIVISION OF APPLIED PHYSICS
BROOKLYN POLYTECHNIC INSTITUTE
BROOKLYN, N. Y.
EDWARD J. FELTEN
IRA BINDER
BEN POST

RECEIVED MAY 16, 1958

(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-

(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).