reaction mixture was maintained by addition of water. The turbid distillate was collected in a cold solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid. This mixture was allowed to stand overnight at 0°, after which the solid was collected by filtration and washed with 2 *N* hydrochloric acid followed by water. The *p*-toluenethiol was separated by allowing the resulting solid to stand in a vacuum desiccator over moist sodium hydroxide pellets for 2.5 days. The sodium hydroxide was then dissolved in water, the solution filtered, the ice-cold filtrate acidified with hydrochloric acid and the resulting *p*-toluenethiol removed by filtration; yield 118 mg. (33%), m.p. 41–43°, lit.[23] m.p. 44°. The solid which remained after standing in the desiccator was benzaldehyde 2,4-dinitrophenylhydrazone; yield 768 mg. (93%), m.p. 227–236°, lit.[24] m.p. 235°.

The contents of the distilling flask were filtered, and the filtrate was neutralized with 10% sodium hydroxide solution to liberate aniline. Bromine water was added in slight excess, and the resulting precipitate was removed by filtration, washed with water and dried; 2,4,6-tribromoaniline was obtained as a gray solid; yield 685 mg. (72%), m.p. 118–120°, lit.[25] m.p. 119–120°.

Oxidative Decomposition of VI.—This reaction was carried out under conditions similar to those used by Caldwell and Sayin for oxidation of sulfides.[26] To an ice-cold solution of 869 mg. (2.5 mmoles) of VI in a mixture of 5 ml. each of acetic acid and acetic anhydride was added dropwise with stirring 1 ml. of 30% hydrogen peroxide. The reaction mixture was allowed to stand in an ice-bath overnight and then at 20° for 3 hr. Removal of excess acetic acid–acetic anhydride gave 930 mg. of a viscous yellow residue containing some suspended solid. This material was dissolved in 10 ml. of benzene, and one-half of this solution was chromatographed resulting in the isolation of 151 mg. (89% yield) of acetanilide, m.p. 113–113.5°.[27]

Reaction of I with Benzoyl Chloride–Pyridine.—To a solution of 611 mg. (2.0 mmoles) of I in 5 ml. of anhydrous pyridine and 10 ml. of anhydrous benzene was added dropwise 0.50 ml. (606 mg., 4.3 mmoles) of benzoyl chloride. The resulting mixture was heated in a water-bath at 60–70° for 0.5 hr. and then poured into 100 ml. of water. The benzene phase was separated, and the aqueous phase was extracted with 10 ml. of benzene. The combined benzene solutions were washed successively with several 25-ml. portions of water, 5% sodium carbonate solution and again with water. The benzene solution was diluted to 5 ml. and was chromatographed. The first three fractions gave, after two recrystallizations from ethanol, 154 mg. (34% yield) of colorless *p*-tolyl thiolbenzoate, m.p. 76–76.5°, lit.[11] m.p. 75° (mixed m.p. 76–76.5°).

After two recrystallizations from ethanol, residues from fractions 7–13 gave 36 mg. (9% yield) of colorless benzanilide, m.p. 163–163.5°, lit.[28] m.p. 161–162° (mixed m.p. 163–163.5°).

Acknowledgments.—This investigation was supported in part by a grant (G1100) from the National Science Foundation. Also R.J.M. wishes to express appreciation for a predoctoral fellowship (N-4077) from the National Institutes of Health, Public Health Service, during the tenure of which a part of this work was carried out.

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[23] E. Fischer, *Ber.*, **48**, 93 (1915).

[24] T. Curtius and G. M. Dedichen, *J. prakt. Chem.*, [2] **50**, 241, 264 (1894).

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[27] Oxidation of VI with potassium permanganate solution gave similar result but a lower yield of acetanilide (49%).

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COMMUNICATIONS TO THE EDITOR

KINETICS OF DISPLACEMENT REACTIONS AT THE SULFUR ATOM. II. STEREOCHEMISTRY

Sir:

In bimolecular nucleophilic substitutions at atoms of the second row of the Periodic Table, the problem arises of the structure of the transition state. Recently Sommer and Bennett[1] have examined the reactivity of a bridgehead organosilicon chloride and have tentatively suggested that in direct displacements at silicon the entering group does not necessarily make an angle near 180° with the leaving group and the central atom, but there might be other directions of attack. While awaiting further, more detailed information on this extremely interesting subject we wish to communicate some results which indicate to what extent in direct substitutions at sulfur (and conceivably at other second-row atoms), attack from the back side is favored over attack from other directions.

The reaction under investigation was the isotopic exchange between organic thiosulfates and (S^{35}) sulfite ion

$$\mathrm{R{-}S{-}SO_3^-} + \mathrm{SO_3^{*=}} \rightleftarrows \mathrm{R{-}S{-}SO_3^{*-}} + \mathrm{SO_3^=}$$

for which a mechanism of direct displacement at sulfur previously had been established.[2] The present results concern the α-branched alkyl series, that is, for R = Me, Et, *i*-Pr and *t*-Bu. In water at 25°, *p*H 7.9 and ionic strength of 0.5 these relative rates have been measured[3]:

R =	Me	Et	*i*-Pr	*t*-Bu[4]
$100k/k_{\mathrm{Me}}$	100	50	0.7	0.0006

It appears very reasonable to attribute the observed reactivity differences to steric hindrance at the transition state. This is borne out by the following considerations: (i) the electronic effect of a methyl group β- to the seat of substitution is quite negligible, as might be inferred from the almost equal rates of exchange of sulfite ion with benzyl- and *p*-methylbenzyl thiosulfates,[5] (ii) although the rate consistently decreases along the series, by far the greatest drop occurs between two members of the series (*i*-Pr and *t*-Bu), a behavior characteristic of steric effects, (iii) the reaction under consideration being a direct displacement at sulfur, it is easily seen that the above series of reactions is the sulfur

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[1] L. H. Sommer and O. F. Bennett, THIS JOURNAL, **79**, 1008 (1957).

[2] Part 1: A. Fava and G. Pajaro, *ibid.*, **78**, 5203 (1956).

[3] Under the conditions specified the bimolecular rate constant for the methyl derivative is $k = 2.2 \times 10^{-1}$ (mole/l.)$^{-1}$ sec.$^{-1}$.

[4] Extrapolated from data between 60° and 90°.

[5] A. Fava and A. Iliceto, unpublished results.

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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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-

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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).