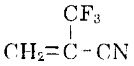
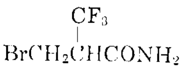
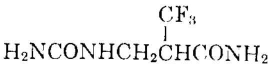

$CH_2{=}\overset{\overset{CF_3}{|}}{C}{-}CN$

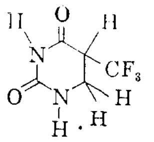
I


$BrCH_2\overset{\overset{CF_3}{|}}{C}HCONH_2$

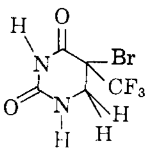
II


$H_2NCONHCH_2\overset{\overset{CF_3}{|}}{C}HCONH_2$

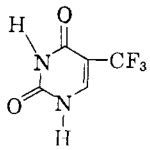
III



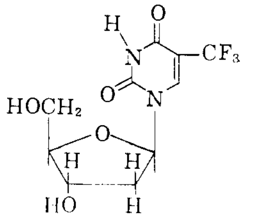
IV



V



VI



VII

NOTE ADDED IN PROOF.—5-Trifluoromethyl-5-hydroxy-5,6-dihydrouracil has been prepared recently by P. W. Feit, *Arch. der Pharmazie*, **295**, 321 (1962). Attempts to convert this dihydrouracil derivative to 5-trifluoromethyluracil were unsuccessful.

Preliminary studies have shown 5-trifluoromethyluracil to be mutagenic to bacteriophage T4[14]; further chemical and biological studies are being carried out with these compounds, and full details of these experiments will be published at a later date.

(14) Dr. Hubert Gottschling, personal communication.

(15) American Cancer Society Professor of Oncology.

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CHARLES HEIDELBERGER[15]
DAVID PARSONS
DAVID C. REMY

RECEIVED JULY 13, 1962

NEW CLASSES OF HIGH MOLECULAR WEIGHT BORON SULFIDES

Sir:

We have discovered two new classes of high molecular weight boron gases comparable to but considerably more numerous than the boron hydrides. These substances were obtained by vaporization from a slightly sulfur-rich, glassy B_2S_3 sample and were identified by mass spectrometry. One class consists of boron sulfides, and the other appears to contain boron, sulfur, and a third element or radical.

The sample, prepared at 700° by the reaction of hydrogen sulfide with elemental boron in silica tubing, followed by flushing with hydrogen and helium to remove most of the excess sulfur, was heated to 300–500° in a graphite Knudsen cell in a Nuclide Analysis Associates 12 inch, 60° magnetic field mass spectrometer having a resolution of about 1000. Ions were formed by impact with 70-volt electrons.

The spectrum consists of clusters of lines which we shall call bands, using spectroscopic notation. The lines arise from the individual isotopic species of a particular chemical formula. The bands have been observed repeatedly and extend to masses higher than 800. Prominent intervals between bands are 11, 32, and 17 (and others by combination) and correspond to the addition of a boron atom, a sulfur atom, and the third element or radical. Although the most intense bands in the spectrum arise from $B_2S_3^+$, the sum of the intensities at higher masses is about twice the intensity of $B_2S_3^+$. The bands decrease in intensity through the 200–300 mass range but increase to a maximum in the 400–500 range.

The ion species in the first class which have been identified are $B_2S_3^+$, $B_2S_4^+$, $B_2S_5^+$, $B_3S_3^+$, $B_3S_4^+$, $B_3S_5^+$, $B_3S_6^+$, $B_4S_6^+$, $B_4S_7^+$, $B_4S_8^+$, $B_5S_6^+$, $B_5S_7^+$, $B_5S_8^+$, $B_5S_9^+$, $B_6S_9^+$, $B_6S_{10}^+$, $B_6S_{11}^+$, $B_7S_{10}^+$, $B_7S_{11}^+$, $B_7S_{12}^+$, $B_7S_{13}^+$, $B_8S_{12}^+$, $B_8S_{13}^+$, $B_8S_{14}^+$, $B_8S_{15}^+$, $B_9S_{13}^+$, $B_9S_{14}^+$, $B_9S_{15}^+$, $B_{10}S_{15}^+$, $B_{10}S_{16}^+$, and $B_{10}S_{17}^+$.

The third component in the second series of compounds has not been firmly identified, but the mass interval of 17 suggests that it is OH. On this basis the observed bands in this system could arise from the ions $B_3S_5OH^+$, $B_3S_6OH^+$, $B_4S_6OH^+$, $B_4S_7OH^+$, $B_5S_8OH^+$, $B_5S_9OH^+$, $B_6S_9OH^+$, $B_6S_{10}OH^+$, $B_7S_{11}OH^+$, $B_8S_{12}OH^+$, $B_8S_{13}OH^+$, $B_3S_{14}OH^+$, $B_9S_{15}OH^+$, $B_9S_{16}OH^+$, $B_{10}S_{15}OH^+$, $B_{10}S_{16}OH^+$, $B_{11}S_{17}OH^+$, and $B_{11}S_{18}OH^+$.

The mass associated with each peak up to about 800 was unambiguously obtained by counting individual lines in numerous spectra. Positive identification of a band was accomplished by comparing the observed relative line intensities with those computed on an IBM 650 computer from the normal isotopic abundance of boron and sulfur.

The boron sulfide species appeared to diminish in comparison with those in the second class as the sample was progressively vaporized. The species containing the most sulfur for a given number of boron atoms also appeared to fall in comparison with those containing less sulfur, in conformity with the suspected congruent vaporization of B_2S_3.

The appearance of such a complex spectrum suggests extensive fragmentation of a larger molecule, but both the change of the relative intensities with time and the spectra obtained with lower energy electrons indicate the presence of many parent species.

The important boron sulfide ions listed above have S/B ratios slightly greater than 1.5 which, when considered in light of the sulfur-rich character of the sample, suggests that the parent molecules may be equilibrium species.

Boron and its compounds exhibit a wide variety of structural and bonding types. It is possible that the large molecules may form boron chains, nets, or icosahedra as are found in the borides. Possibly structures similar to the boron hydrides may be found. More likely, the structures involve rings of alternate boron and sulfur atoms as in $(HBS_2)_3$[1] and perhaps sulfur rings and chains.

The complexity of the molecules in the gas phase suggests the possibility of similar complexity in the liquid phase which may account for the great tendency of boron sulfide samples to form glasses.

Acknowledgments.—We are pleased to acknowledge the generous support of the U. S. Atomic Energy Commission (Contract AT(11-1)-1140), the

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(1) E. Wiberg and W. Sturn, *Z. Naturforsch.*, **8b**, 529 (1953).

help of Mr. Lary L. White who wrote the computer program, and helpful discussions with Dr. Thomas A. Milne. We appreciate the willingness of Prof. John L. Margrave of the University of Wisconsin to allow the use of samples that were prepared by F. T. G. while a graduate student under his direction.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KANSAS FRANK T. GREENE
LAWRENCE, KANSAS PAUL W. GILLES

RECEIVED JULY 23, 1962

EVIDENCE FOR DUAL AND DISTINCT MECHANISMS IN THE SOLVOLYSIS OF 2-OCTYL BROSYLATE IN AQUEOUS DIOXANE

Sir:

Solvolysis of optically active 2-octyl brosylate in 75 volume per cent. aqueous dioxane at 65° furnished, in addition to small amounts of olefins, the expected inverted alcohol of 77% optical purity.[1,2] However, when solvolysis was conducted in the presence of 0.0307 *M* sodium azide the resulting inverted 2-octanol, formed now in competition with 2-octyl azide, proved to be *100% optically pure.* Thus *sodium azide is influencing the stereochemical course of the solvolysis reaction.* These and other pertinent data are summarized in the table.

TABLE I
SOLVOLYSES OF 2-OCTYL BROSYLATE[a] IN 75 VOLUME PER CENT. AQUEOUS DIOXANE AT 65°

$[NaN_3]$ × 10^2	$[\alpha]_{ROH}$[b,c]	$[\alpha]_{RN_3}$[c]	Azide,[d] %	k,[e] sec.$^{-1}$ × 10^5
...	16.9	...	..	23.8 ± 0.2
0.633	14.5	52.0	8.8	23.3 ± 1.0
1.27	16.7[f] 16.3[f]	84.3	26.4	33–26
1.26	16.8	89.9	..	...
3.07	23.5	120	64.9	...
3.07	22.9	130	..	...
6.18	22.0	125	77.6	109 ± 5

[a] [ROBs] = 0.0176–0.0180 *M.* [b] Authentic, optically pure 2-octanol was found to have $[\alpha]^{365}_{25}$ 21.9 ± 0.1. [c] Products were inverted in all cases. Specific rotations measured at 365 mμ, 25°, in 75 volume per cent. aqueous dioxane on a Rudolph, modified Model 200, Photoelectric Polarimeter. [d] Percentage of alkyl azide formed; determined from titration data. [e] Rates (integrated) of acid production determined by titration. The run at 0.0127 *M* NaN_3 displayed a downward-drifting rate constant reflecting a competing SN2 displacement by azide ion. [f] Duplicate determinations.

We interpret these data to mean that *two distinct paths* are followed in the solvolysis of 2-octyl brosylate in the absence of salt: a nucleophilic SN2 displacement by water to furnish inverted alcohol[3]; and a second mode for reaction involving the formation of an intermediate which subsequently reacts to furnish racemic or retained alcohol. The function of the azide, presumably, is to react preferentially with this intermediate to form alkyl azide, thus preventing its conversion to alcohol. The nature of the intermediate has not as yet been positively identified although it is probably either a solvated carbonium ion or an oxonium ion formed in a nucleophilic SN2 displacement by dioxane.[4] Experiments are in progress to choose between these alternatives. In either event these results would seem to have far-reaching implications concerning the long-standing question of the merging of SN1 and SN2 processes.[5] We hope to report on this question and on other aspects of this work in the near future.

Acknowledgment.—This work was supported in part by a grant from the Army Research Office (Durham) and this assistance is gratefully acknowledged.

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[1] The product alcohol has been shown to be optically stable under the reaction conditions.

[2] Alcohol was isolated from the reaction mixture by extraction into pentane, concentration, and purification by gas chromatographic separation.

[3] Inversion of configuration in such solvent-substrate reactions appears to be quite general; see, *e.g.*, A. Streitwieser, Jr., and A. C. Waiss, Jr., *J. Org. Chem.*, **27**, 290 (1962).

[4] Evidence already has been deduced for the intermediacy of oxonium ions in the solvolysis of primary alkyl sulfonates; see A. Streitwieser, Jr., and S. Andreades, *J. Am. Chem. Soc.*, **80**, 6553 (1958).

[5] See, for example, M. L. Bird, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 634 (1954); S. Winstein, E. Grunwald and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951); V. Gold, *J. Chem. Soc.*, 4633 (1956).

[6] Correspondence should be addressed to this author.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY HENRY WEINER
LAFAYETTE, INDIANA RICHARD A. SNEEN[6]

RECEIVED JUNE 26, 1962

SILICON-SILICON BOND DISSOCIATION ENERGIES IN DISILANE AND HEXACHLORODISILANE[1]

Sir:

Bonds formed by silicon to other elements are generally stronger than those formed by carbon. Moreover, chemical evidence exists suggesting that silicon–silicon bonds are in some cases more stable thermally than corresponding carbon–carbon bonds.[2] Limited thermochemical data for the silicon–silicon bond, on the other hand, have given the impression that this bond is considerably weaker than a carbon–carbon bond. Thus, a thermochemical bond energy E(Si–Si) = 46.4 kcal. mole^{-1} has been calculated for disilane,[3] and the activation energy for pyrolysis of disilane has been taken to imply a value for $D(H_3Si–SiH_3)$ of ~50 kcal. mole^{-1}.[4,5] For ethane $D(H_3C–CH_3)$ = 83 kcal. mole^{-1}.[4] We have now measured the dissociation energies of the silicon–silicon bonds in disilane and hexachlorodisilane by electron impact, and have found that they are comparable in strength to carbon–carbon bonds.

A commercial sample of hexachlorodisilane was purified for use by high vacuum distillation and a sample of disilane was kindly provided by Professor M. Kent Wilson. The appearance potentials were

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[1] This study was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

[2] A. G. MacDiarmid, "Advances in Inorganic Chemistry and Radiochemistry," Eds., H. J. Emeléus and A. G. Sharpe, **3**, 207 (1961).

[3] S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 779 (1961).

[4] See T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths, London, 1958, and references cited therein.

[5] It has been pointed out (reference 4) that the mechanism for pyrolysis of disilane has not been elucidated and may not proceed *via* formation of silyl radicals. Moreover, even if the initial reaction step is $Si_2H_6 \rightarrow SiH_3 + SiH_3$, the activation energy of the recombination reaction may not be zero. Only if this is true will the activation energy of pyrolysis be equal to the bond dissociation energy.