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.

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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°

$[NaN_3] \times 10^2$	$[\alpha]_{ROH}$[b,c]	$[\alpha]_{RN_3}$[c]	Azide,[d] %	k,[e] sec.$^{-1}$ $\times 10^5$
...	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 S_N2 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 S_N2 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 S_N2 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 S_N1 and S_N2 processes.[5] We hope to report on this question and on other aspects of this work in the near future.

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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).

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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 $E(\text{Si–Si}) = 46.4$ 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 $D(H_3Si\text{–}SiH_3)$ of $\sim$50 kcal. mole^{-1}.[4,5] For ethane $D(H_3C\text{–}CH_3) = 83$ 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.