

postulate of mechanism 1 in which $k_{inv} \gg k_2$ for the racemization studies described, and amount to the following.

(1) Optically active R_3Si^*F in pentane and *t*-butyl alcohol solvents is racemized by added methanol with-out displacement of $-F$.

(2) Such racemization cannot be due to fluoride-fluoride exchange engendered by formation of a small amount of HF. Addition of HF to the reaction medium strongly retards the rate of racemization.

(3) Such racemization cannot be due to the formation of ionic intermediates containing ionized fluorine. The high bond energy of Si-F and the low dielectric constants of the *t*-butyl alcohol and pentane solvents argue against such a possibility. Furthermore, in pure formic acid, a solvent of high ionizing power, the pseudo first-order rate constant for racemization of R_3Si^*F is only $3.7 \times 10^{-3} \text{ min.}^{-1}$, compared to $3.5 \times 10^{-2} \text{ min.}^{-1}$ in pentane containing 0.580 *M* methanol. Also, ionic intermediates containing ionic fluorine should be considerably stabilized by the presence of HF, due to probable formation of HF_2^- from such intermediates. Instead, rate-retardation is observed when HF is added.

Polarimetric rate data for racemization of R_3Si^*F (0.0358 *M*) in pentane by methanol (0.580 *M*) at 31.2° give a linear first-order plot, $k_1 = 3.5 \times 10^{-2} \text{ min.}^{-1}$. When racemization of an equimolar mixture of R_3Si^*F and optically active $R_3Si^*OCH_3$ (0.0179 *M* in each component) was carried out, the optical rotation only decreased to the expected value for the optically active methoxysilane and remained constant at that value for 26 hr. Thus, the racemization of the fluorosilane does not involve the methoxysilane as an intermediate, and racemization proceeds without displacement of fluoride ion. In the presence of HF ($7.5 \times 10^{-4} \text{ M}$), and keeping the methanol and fluorosilane concentrations constant, the rate constant for racemization decreased from $3.5 \times 10^{-2} \text{ min.}^{-1}$ to $4.0 \times 10^{-5} \text{ min.}^{-1}$, by a factor of almost 10^3 . In pentane solvent, racemization rate increases rapidly with increasing methanol concentration. Indeed, the order of reaction with respect to methanol was found to be approximately 4. In an extremely nonpolar solvent such as pentane, this does not mean that four molecules of methanol are covalently bonded to R_3Si^*F in the rate-controlling transition state.

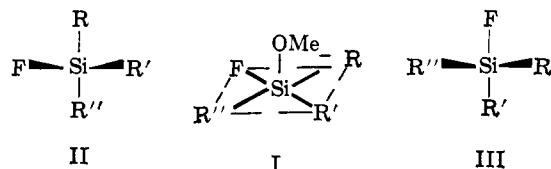
The rate data for racemization of R_3Si^*F (0.0358 *M*) in *t*-butyl alcohol by methanol (2.06 *M*) at 25° give a linear first-order plot, $k_1 = 2.0 \text{ min.}^{-1}$. In *t*-butyl alcohol solvent, as in pentane, an equimolar mixture of R_3Si^*F and $R_3Si^*OCH_3$ was racemized by methanol only to the point of complete racemization of R_3Si^*F and zero racemization of $R_3Si^*OCH_3$. Both HF ($8.44 \times 10^{-2} \text{ M}$) and boron trifluoride etherate (0.529 *M*) retard racemization of R_3Si^*F by methanol in the *t*-butyl alcohol solvent, the former by a factor of 17 and the latter by a factor of 4, for $[R_3Si^*F]$ equal to 0.0358 *M* and $[CH_3OH]$ equal to 0.580 *M*. Further studies are in progress.⁶

Addition of methoxide ion (from $MeOH_2^+ - MeO^-$) to the central silicon to give a geometrical arrangement in which R, R', R'', and F are coplanar constitutes a possible mechanism for the racemization.⁷ For a pen-

(6) Based on a solvolysis study of Ph_3SiF and *p*-tolyls SiF in acetone-water (C. G. Swain, R. M. Esteve, and R. H. Jones, *J. Am. Chem. Soc.*, **71**, 965 (1949)), an expanded-octet mechanism was proposed for these reactions, but the evidence was inconclusive. It was also consistent with an SN_2 mechanism in which bond-formation exceeds bond-breaking in the rate controlling transition state. On the basis of the present stereochemical results and others, we now believe that the original mechanism postulate of Swain and co-workers for the solvolyses was probably correct.

(7) Structure I may also derive from reaction of R_3Si^*F with two molecules of methanol. In either case addition of HF should decrease the basicity of the medium and decrease rate. It is probable that I exists as one

tacovalent intermediate, the organic groups and the fluorine would be *basal* in the tetragonal pyramid and methoxide would be *apical*. Such an intermediate (I) would be optically active and could return to R_3Si^*F with *retention* or *inversion* of configuration, depending upon which pair of *trans* groups (R and R'' or R' and F) move toward the methoxy group as it leaves. In I the silicon atom need not be coplanar with R, R', R'', and F.



Structure III, resulting from movement of R and R'' toward MeO^- , is the enantiomer of structure II which results from movement of R' and F toward MeO^- .

An octahedral, hexacoordinate silicon intermediate, Si, R, R', R'', and F coplanar, which would be optically inactive if it contained *trans* methoxy groups, is also possible but seems less likely at present.

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component of an ion-pair which also contains $MeOH_2^+$ and that one or more molecules of methanol stabilize the ion-pair by solvation.

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Segregation of Benzoic Acid-*d* from Benzoic Acid by Zone Melting

Sir:

In an attempt to identify impurities segregated from benzoic acid by zone melting, the mass spectra of various fractions of zone-melted ingots were examined. It was found that samples taken from the tops of zone-melted ingots showed smaller ratios of mass 123 to mass 122 than did the original acid. The samples did not seem to contain any impurity in an amount that would account for the observed ratios. It was thought that isotopic fractionation might be responsible, and to test this the following experiment was carried out.

Benzoic acid-*d* (0.50 g., 95% isotopic purity) was mixed with 19.20 g. of benzoic acid that had been purified by zone melting, recrystallization from water, and sublimation. The mixture was melted in a sealed zone melting tube, shaken vigorously, and allowed to solidify.

The ingot was subjected to 274 passes in an automatic zone refiner.¹ Deuterium was determined by the infrared technique of Jones and MacKenzie² in samples taken from three points in the ingot. The top, middle, and bottom of the ingot gave water containing 0.23, 0.36, and 0.43 mole % D_2O , respectively. The original mixture contained 0.33 atom % deuterium. It is clear that $C_6H_5CO_2D$ is distributed in $C_6H_5CO_2H$ as an impurity whose distribution coefficient³ is less than unity.

Benzoic acid and benzoic acid-*d* probably form a continuous series of solid solutions. Since the melting point of $C_6H_5CO_2H$ is about 3° higher than that of $C_6H_5CO_2D$,⁴ it would be expected that the melting point of the former would be depressed by admixture with the latter. The observed distribution is consistent with this situation.

(1) G. J. Sloan and N. H. McGowan, *Rev. Sci. Instr.*, **34**, 60 (1963).

(2) R. N. Jones and M. A. MacKenzie, *Talanta*, **3**, 356 (1960).

(3) W. G. Pfann, "Zone Melting," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 2.

(4) J. M. Robertson and A. R. Ubbelohde, *Proc. Roy. Soc. (London)*, **A170**, 222 (1939).

We have also observed segregation of deuterated species in a number of amides, but not, for example, in hydrocarbons. Thus, it appears that the segregation depends on the presence of hydrogen-bonded hydrogens.

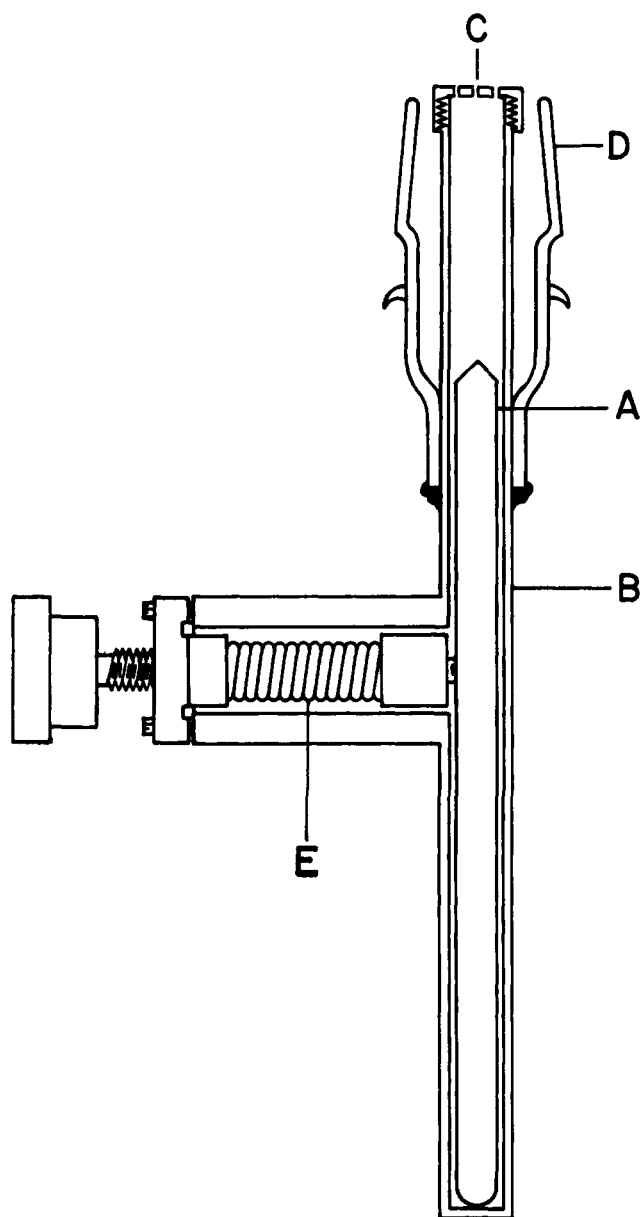


Fig. 1.—Modified tube breaker.

The analytical method of Jones and MacKenzie involves the combustion of an organic compound with copper oxide in a sealed quartz tube which must be broken in an evacuated system to recover the water formed. The tube breaker described by these workers was found to be inconvenient, since it often leaked when the vacuum distillation system was baked. The tube breaker shown in Fig. 1 is easily made, inexpensive, and very reliable. Quartz tube A, containing combustion products of a deuterated sample, is slipped into brass sleeve B, and the latter is closed by means of perforated cap C. The assembly is attached to a distillation manifold by standard-taper joint D which is permanently connected to B by epoxy resin cement. Tube A is broken by advancing the bellows mechanism E of an all-metal vacuum valve (Vacuum-Electronics Corporation, Cat. No. R12P) which is sealed with an

O-ring made of Teflon polytetrafluoroethylene resin. Quartz fragments are retained by C.

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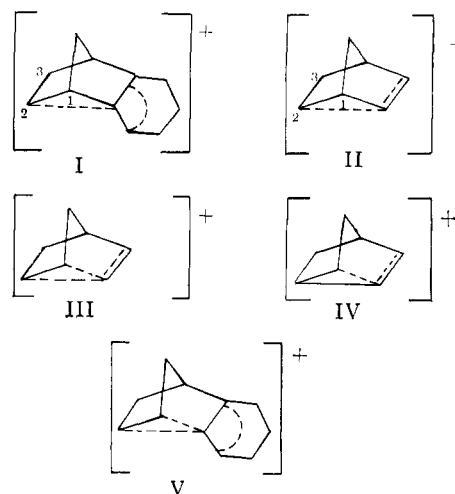
G. J. SLOAN

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Racemization in the Solvolysis of *exo*-2-Benznorbornenyl Brosylate

Sir:

Interest in the nature of intermediate ions in reactions of norbornyl derivatives has remained at a high level.¹ We wish to report racemization accompanying the solvolysis of *exo*-2-benznorbornenyl brosylate, a finding incompatible with the previously postulated nonclassical intermediate I.²



Optically active *exo*-2-benznorbornenol was prepared from benznorbornadiene³ and diisopinocampheylborane,⁴ which was obtained from hydroboration of α -pinene of $[\alpha]^{27D} + 46.8 \pm 0.05^{5,6}$ by the procedure of Sondheimer and co-workers.⁷ *exo*-2-Benznorbornenyl acetate of $[\alpha]^{25D} - 2.00 \pm 0.05^{5,6}$ was prepared using acetic acid in pyridine to avoid possible acid-catalyzed rearrangements. The alcohol was regenerated by lithium aluminum hydride reduction of the acetate, and the brosylate was prepared as previously.² Solvolysis of the brosylate at 50° was carried out in glacial acetic acid containing 0.1 M sodium acetate for 18 hr. (well over ten half-lives²), yielding acetate of $[\alpha]_D 0.000 \pm 0.001^{5,8}$ indicating more than 99.9% racemization. Thus it is clear that the reaction proceeds through a symmetric intermediate.

The homobenzylic ion I predicts complete retention of configuration and of optical activity. Racemization could occur through an intermediate in which carbon atoms 2 and 3 or 2 and 1 become equivalent. These results are reminiscent of the rearrangement in the

(1) For recent examples, see: H. C. Brown and F. J. Chloupek, *J. Am. Chem. Soc.*, **85**, 2322 (1963); H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963); S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963); P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, *ibid.*, **85**, 479 (1963); H. Tanida, *ibid.*, **85**, 1703 (1963).

(2) P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960).

(3) G. Wittig and E. Knauss, *Ber.*, **91**, 895 (1958).

(4) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 486 (1961).

(5) We gratefully acknowledge the gift of the optically active α -pinene from H. I. Enos, Jr., Hercules Powder Co., Wilmington, Del.

(6) Readings were taken with a Kern polarimeter using pure liquid in a 2-dm. tube. Uncertainties are average deviations from the mean of ten readings.

(7) S. Wolfe, M. Nussim, Y. Mazur, and F. Sondheimer, *J. Org. Chem.*, **24**, 1034 (1959).

(8) We are grateful to Mr. Kenneth D. Stevens, University of Washington, for this reading taken with a Bendix automatic polarimeter using a 25% chloroform solution.