

Fig. 1.—Pressure dependence of helix content f for poly-L-glutamic acid in 0.2 M NaCl: temperature (O) 10°, (⊖) 20°, (●) 25°, (⊕) 20° in dioxane–water (1:2); indicated pH values were measured at room temperature; solid curve was calculated from eq. 1 and 2 with $\sigma = 0.005$, $\Delta\bar{V} = 1$ cc./mole.

as solvent at pH 5, a condition in which $f = 1$ and in which the turbidity that complicates measurements in pure aqueous solution at low pH is absent.

As shown elsewhere,⁵ f is related to the stability constant s and the helix interruption constant σ by the equation

$$f = \frac{1}{2} + \frac{s - 1}{2[(1 - s)^2 + 4\sigma s]^{1/2}} \quad (1)$$

From eq. 1 we find

$$\left(\frac{\partial f}{\partial P}\right)_T = -\frac{\sigma s(1 + s)\Delta\bar{V}}{RT[(1 - s)^2 + 4\sigma s]^{3/2}}, \quad (2)$$

where $\Delta\bar{V}$ is the change in partial molal volume of the residue on going from random coil to helix, and is equal to $-RT(\partial \ln s/\partial P)_T$. It is assumed here that σ is independent of pressure, *i.e.*, that no volume change occurs on formation of an interruption by a process that maintains a constant number of hydrogen bonds.⁵

The change in f over the 130-atm. range was 1–2% near the center of the transition, and $(\partial f/\partial P)_T$ was therefore essentially constant in this range for a given solution. On some solutions measurements were at both 10 and 20° in order to determine whether σ is sensitive to temperature. The experimental data are plotted in Fig. 1, with $(\partial f/\partial P)_T$ corrected, as shown, to 10° in order to remove any temperature dependence other than what may be contained in σ and $\Delta\bar{V}$.

A value of σ was obtained for each set of experimental conditions by simultaneous solution of eq. 1 and 2. An IBM 1620 computer aided in this calculation. $\Delta\bar{V}$ was taken as 1 cc./residue mole as found by Noguchi and Yang³ for this system. The average value of σ thus obtained was $(5 \pm 2) \times 10^{-3}$. The theoretical curve of $(\partial f/\partial P)_T$ vs. f , using this value of σ , is seen in Fig. 1 to lie essentially within experimental error of all of the points. Assuming that $\Delta\bar{V}$ does not vary, we conclude that σ is insensitive to temperature, as previously expected.⁵

The above value for σ stands in contrast to the value 2×10^{-4} for poly- γ -benzyl-L-glutamate (PBLG) in a

mixed organic solvent,⁶ and does not support Zimm and Bragg's hypothesis⁷ that this quantity should be independent of the side chain and solvent. While Zimm and Rice⁸ interpreted titration data on PGA as giving support to the hypothesis, they recognized room for error in this interpretation. We conclude that the practice of using a single value for all polypeptides should be abandoned, since it is at best a very rough approximation.

The cooperativeness of the helix-coil transition can be visualized from the tendency for hydrogen bonds to group together in uninterrupted sequences. The average number of bonds in such a sequence has been shown⁵ to be $1 + \sigma^{-1/2}$. This number is 15 for PGA, as compared with 72 for PBLG. The former is less cooperative than the latter, and this is one factor contributing to the gradualness observed for the thermal transition in PGA.^{9,10}

Some of the data in Fig. 1 were taken on a single solution at two different temperatures. The decrease in f upon heating is similar in magnitude to that found by Fasman, *et al.*,¹⁰ in a more extensive study of the temperature effect in the same system at pH 4.88. Their data, as well as ours, yield a value of -630 cal./residue mole for the enthalpy of helix formation, which is essentially constant from pH 4.88 to 5.08. This value is an order of magnitude larger than some previous estimates,⁵ due in part to the larger value of σ found here. The entropy of helix formation is -2.0 cal./deg./residue mole, and is likewise larger than previous estimates.

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(6) B. H. Zimm, P. Doty, and K. Iso, *Proc. Natl. Acad. Sci. U. S.*, **45**, 1601 (1959).

(7) B. H. Zimm and J. K. Bragg, *J. Chem. Phys.*, **31**, 526 (1959).

(8) B. H. Zimm and S. A. Rice, *Mol. Phys.*, **3**, 391 (1960).

(9) P. Doty, A. Wada, J. T. Yang, and E. R. Blout, *J. Polymer Sci.*, **23**, 851 (1957).

(10) G. D. Fasman, C. Lindblow, and E. Bodenheimer, *J. Am. Chem. Soc.*, **84**, 4977 (1962).

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The Solvolysis of 7-*anti*-Bromo-2-*exo*-benzenesulfonamidobicyclo[2.2.1]heptane. An Example of Solvolytic Ring Opening

Sir:

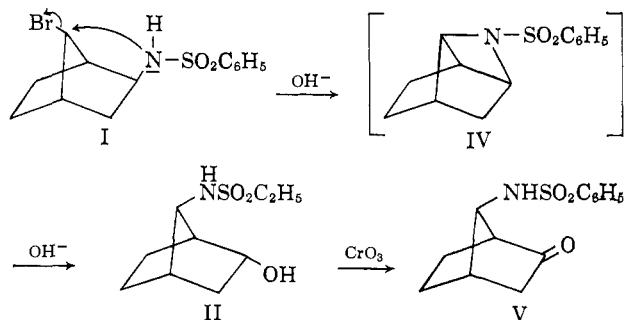
When 7-*anti*-bromo-2-*exo*-benzenesulfonamidobicyclo[2.2.1]heptane (I), the preparation of which is described elsewhere,¹ was refluxed for 25 hr. in an aqueous methanolic solution containing excess sodium carbonate, there was obtained 2-hydroxy-7-*syn*-benzenesulfonamidobicyclo[2.2.1]heptane (II) as the minor product and 3-cyclopentenylacetaldehyde (III) as the major product.

The formation of II can be visualized as occurring by backside displacement of the 7-*anti* bromine by the 2-*exo*-benzenesulfonamido group to give intermediate

(5) J. Applequist, *J. Chem. Phys.*, **38**, 934 (1963).

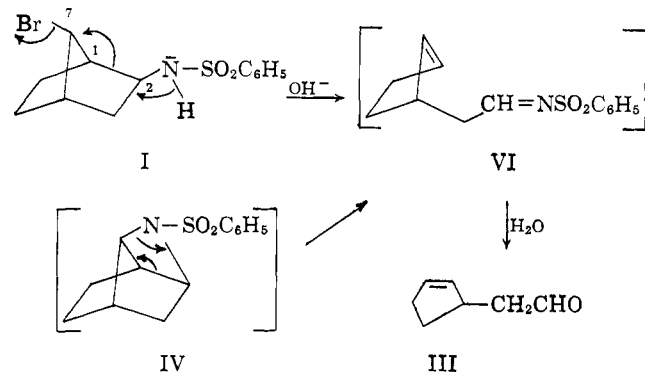
(1) A. C. Oehlschlager and L. H. Zalkow, *Tetrahedron Letters*, in press.

azetidine (IV) which under the reaction conditions is opened by hydroxide ion to give II. Participation of a suitable 2-*exo* group in the solvolysis of 7-*anti* substituents might be expected in view of the known pronounced acceleration of solvolysis shown in 7-*anti*-norbornenyl systems.² However, the 2-methylene substituent was ineffective in this regard.³ II was characterized by its oxidation with Jones reagent⁴ to give



the known ketone V⁵ and the hydroxyl group in II is assumed to be in the *endo* configuration.

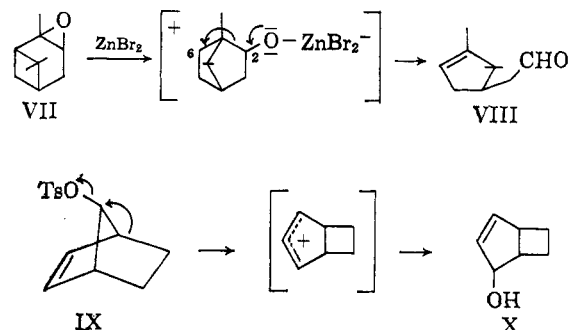
The major product III undoubtedly arises by hydrolysis of VI, the latter presumably being produced either directly from I by cleavage of the C₁-C₂ bond as depicted, or from intermediate IV, which may suffer collapse of the strained azetidine ring under the re-



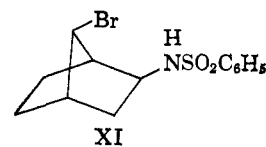
action conditions. The former path is analogous to solvolytic fragmentation reactions of amines studied by Grob.⁶ Aldehyde III was identified by elemental analysis of its 2,4-DNP (C₁₃H₁₄N₄O₄, m.p. 100-101°, lit.⁷ m.p. 98-99°) and by the characteristic n.m.r. spectrum of the 2,4-DNP which showed six methylene protons (δ 1.2-2.6), one methinyl proton (δ 3.0), two olefinic protons (δ 5.75), and one aldehydic proton (δ 8.84).

Berson² has pointed out that formal cleavage of a bicyclo[2.2.1]heptane has been reported in only a few cases and this is believed to be the first example in which cleavage occurs by displacement at C₇ giving a double bond at the C₁-C₇ position of the original norbornane skeleton. The reported conversion⁸ of α -pinene oxide (VII) to campholenic aldehyde (VIII) is somewhat

analogous, but involves displacement at C₆. Internal displacement at C₇ has been observed in the hydrolysis of *syn*-7-norbornenyl *p*-toluenesulfonate (IX) to yield 2-bicyclo[3.2.0]heptenol-4 (X). In the latter case, the formation of a stabilized intermediate allylic carbonium ion provides a strong driving force for the ring cleavage.



In contrast to the solvolysis of I, as described above, the isomeric 7-*syn*-bromo-2-*exo*-benzenesulfonamidobicyclo[2.2.1]heptane¹ (XI) was quantitatively recovered



unchanged after refluxing in 5% aqueous alcoholic sodium hydroxide for 60 hr.; thus it is apparent that participation by the benzenesulfonamido group must occur in the cleavage of the C-Br bond in I.

(9) National Defense Education Act Fellow, 1962-1965.

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The Structure of the Decavanadate Ion¹

Sir:

When vanadate solutions (V₂O₅ dissolved in alkali) are acidified to a pH value between 2 and 6, they turn orange in color because of the formation of the isopolycomplex ion, V₁₀O₂₈⁶⁻. Salts of this decavanadate ion are readily crystallized from such solutions by evaporation, and at least two, Ca₃V₁₀O₂₈·16H₂O (pascoite) and K₂Mg₂V₁₀O₂₈·16H₂O (hummerite) occur naturally in the Colorado Plateau vanadium-uranium ore deposits.² The devanadate ion in solution has been established chemically³ to be a 10-nucleate molecular group. Its structure has now been revealed for the first time by simultaneous and entirely independent crystal structure analysis of pascoite (at N.R.C.) and of the zinc analog of hummerite, K₂Zn₂V₁₀O₂₈·16H₂O (at U.S.G.S.). Crystals of pascoite are monoclinic, I2/m, while those of the zinc analog of hummerite are triclinic, P $\bar{1}$. Both structures have been solved by three-dimensional Patterson and Fourier methods and are being refined by least-squares procedures.

In both crystals the decavanadate group may be described in terms of a portion of the rock salt type

(2) J. A. Berson, "Carbonium Ion Rearrangements in Bridged Bicyclic Systems," in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

(3) E. van Tamelen and C. I. Judd, *J. Am. Chem. Soc.*, **80**, 6305 (1958).

(4) A. Bowers, T. H. Halsall, E. R. H. Jones, and A. J. Iemin, *J. Chem. Soc.*, 2555 (1953).

(5) L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, **28**, 3303 (1963).

(6) C. A. Grob, *Gazz. chim. ital.*, **92**, 902 (1962).

(7) C. W. Whitehead, et al., *J. Org. Chem.*, **26**, 2814 (1961).

(8) B. Arbusov, *Ber.*, **68**, 1430 (1935).

(1) Publication approved by the Director, U. S. Geological Survey.

(2) H. T. Evans, Jr., M. E. Mrose, and R. Marvin, *Am. Mineralogist*, **40**, 314 (1955); in this abstract, for pascoite, C2/M should read I2/m.

(3) F. J. C. Rossotti and H. Rossotti, *Acta Chem. Scand.*, **10**, 957 (1956).