homouridine-6′-phosphonic acid (VIIa), mp 198–199° (from ethanol), in 84% yield from Va; $\lambda_{max}^{H_2O}$ 263 mμ (ε 10,000). The product was homogeneous by paper chromatography and electrophoresis under a variety of conditions and behaved much like uridine 5′-phosphate. The over-all yield of crystalline VIIa from 2′,3′-O-isopropylideneuridine was 41%.

In a similar series of reactions 2′,3′-O-isopropylideneadenosine-5′-carboxaldehyde (Ib, prepared *in situ*[2a]) was treated with II to give the unsaturated phosphonate ester IIIb in 33% yield. This product was obtained as a foam which has resisted crystallization. Catalytic hydrogenation of IIIb was extremely slow and incomplete even after prolonged treatment with several portions of fresh catalyst. Reduction was readily achieved using 5 equiv of diimide generated from potassium azodicarboxylate and acetic acid in pyridine.[9] The resulting saturated phosphonate IVb was obtained as needles, mp 135–136° (from benzene), in 69% yield. Transesterification with sodium benzoxide as above gave the dibenzyl ester Vb, mp 127–128°, in 75% yield, and subsequent catalytic hydrogenolysis rapidly removed both ester groups, giving the isopropylidenephosphonic acid VIb as a syrup in essentially quantitative yield. Conditions necessary for the removal of the isopropylidene group inevitably led to some hydrolysis of the glycosidic bond with release of adenine. Following treatment of free acid VIb in water at 100° for 70 min, the mixture was purified by ion-exchange chromatography on DEAE-Sephadex (HCO_3^-), giving the monotriethylammonium salt of VIIb in 62% yield. Acidification of a solution of the latter in aqueous ethanol gave crystalline 6′-deoxyhomoadenosine-6′-phosphonic acid (VIIb), mp 170–172° dec, $\lambda_{max}^{H_2O}$ 259 mμ (ε 14,000).

Satisfactory condensations of the ylide II with other ribo- and deoxyribonucleoside-5′-carboxaldehydes have also been achieved, and several 6′-deoxyhomonucleoside-6′-phosphonic acids have been converted into analogs of natural nucleoside polyphosphates, nucleoside coenzymes, and related compounds.[10] Details of these syntheses and of enzymatic studies on the resulting compounds will be described shortly.

(9) J. W. Hamersma and E. I. Snyder, *J. Org. Chem.*, 30, 3985 (1965).
(10) Unpublished studies by U. Brodbeck, G. H. Jones, and J. G. Moffatt.

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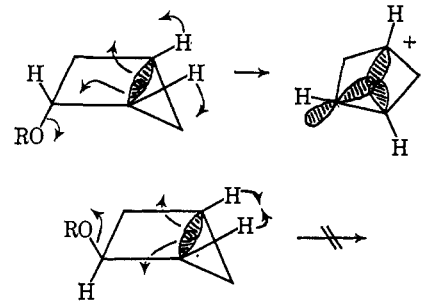
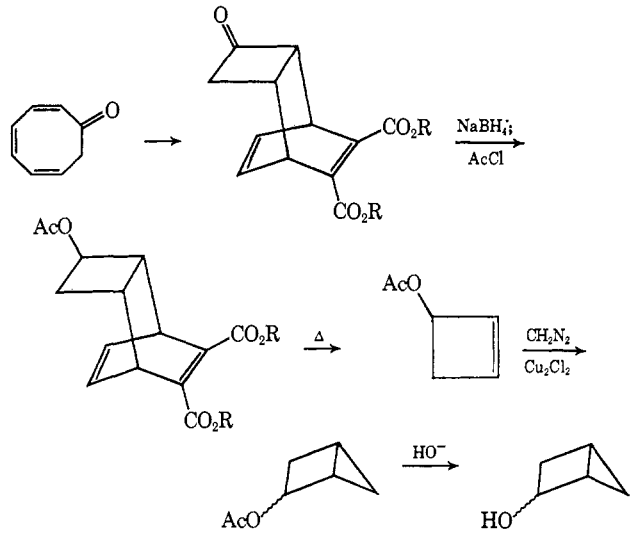
Solvolysis of Bicyclo[2.1.0]-2-pentyl Derivatives[1]

Sir:

The bicyclo[2.1.0]-2-pentyl derivatives should provide another valuable test of the cyclobutyl orbital participation scheme which we found useful in explaining the solvolytic reactions of the *cis*- and *trans*-fused bicyclo[4.2.0]-7-octyl tosylates.[2] The *endo* isomer would be expected to be quite reactive, for the required orbital rotation will relieve part of the strain caused by the central bond. The *exo* isomer would be expected to be much less reactive because the required rotation would lead to an increase in strain. Participation by one of the nonbridging cyclobutyl bonds might also be involved, but this would not lead to as much strain relief.



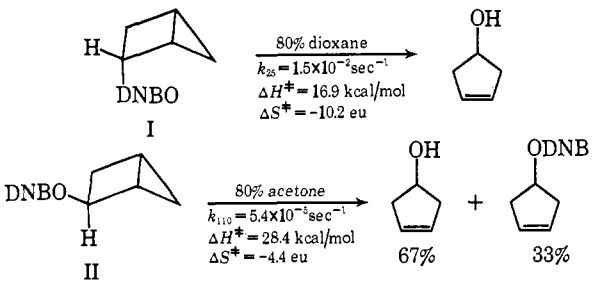
The alcohols were prepared by forming the Diels–Alder adduct between cyclooctatrienone and ethyl acetylenedicarboxylate,[3] followed by sodium borohydride reduction, acetylation, pyrolysis, and treatment with diazomethane catalyzed by cuprous bromide.



The mixture of epimeric alcohols could be separated with some difficulty by vpc. The assignment of configuration was made by an analysis of the nmr spectrum. The spectrum of one isomer had seven distinct multiplets, one for each of the protons. By decoupling experiments and computer simulation of the spectrum, the coupling constant of the hydrogen α to the bridgehead hydrogen was found to be 4.2 Hz.[4] In the cyclobutane ring the coupling constant between the bridgehead proton and an *endo* proton was found to be 0.5 Hz, whereas that to the *exo* proton was 4.0 Hz. Thus, the above isomer has an *endo*-hydroxy group. Similarly, the spectrum of the other isomer indicated a much smaller coupling constant to the bridgehead proton.

The rate constants and products of the solvolysis of the 3,5-dinitrobenzoates derived from the two alcohols are shown below.[5] The extrapolated rate constant for

(1) This investigation was supported by Public Health Service Grant GM12800 from the National Institute of General Medical Science.
(2) K. B. Wiberg and J. G. Pfeiffer, *J. Am. Chem. Soc.*, 90, 5324 (1968).
(3) A. C. Cope, S. F. Schaeren, and E. R. Trumbull, *ibid.*, 76, 1096 (1954).
(4) The analysis of the nmr spectrum was carried out by D. Barth and will be reported in detail at a later time. We thank him for supplying us with his data.
(5) Because of analytical difficulties, the solvolysis of the *endo* isomer was studied in aqueous dioxane rather than the more common aqueous acetone. The *Y* values of 80% acetone and 80% dioxane are almost the same, and so there should be a negligible difference in rate between the two solvents.



II is 1.0×10^{-9} sec^{-1} at 25°. This leads to a ratio of rates of reaction of 10^7:1 for I and II. Since the same product is formed from each compound, it is clear that thermodynamic factors are not involved in the difference in reactivity.

The rate of reaction of II is similar to that of *t*-butyl 3,5-dinitrobenzoate ($k_{110} = 4.31 \times 10^{-5}$ sec^{-1}) and spiro[4.2]-2-heptyl dinitrobenzoate ($k_{110} = 2.70 \times 10^{-4}$ sec^{-1}).[6] It also appears to be essentially the same as that for northujyl *p*-nitrobenzoate.[7] The reactivity of II is then normal for a secondary cyclopropylcarbinyl derivative.

The marked acceleration found with I must be due to strain relief in the activated complex. The difference in activation enthalpy between I and II (12 kcal/mol) is nearly half the strain relief on going from bicyclo[2.1.0]-pentane to cyclopentene.[8] Thus, the process depicted above must have occurred to a large extent in the formation of the activated complex for I. The experimental results are then in excellent agreement with the expectations based on the orbital participation scheme.

(6) K. B. Wiberg and J. E. Hiatt, *Tetrahedron Letters*, 3009 (1968).
(7) From the data given by L. Birlandeanu, T. Hanafusa, B. Johnson, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 2316 (1966); we estimate a rate constant of 1×10^{-9} sec^{-1} at 25°.
(8) From the heat of hydrogenation of bicyclopentane (R. B. Turner, "Kekule Symposium," Butterworth & Co. (Publishers) Ltd., London, in press, p 67) one obtains $\Delta H_f = 36.6$ kcal whereas $\Delta H_f = 7.9$ kcal for cyclopentene ("Selected Values of Properties of Hydrocarbons," API Project 44, Carnegie Institute of Technology, Pittsburgh, Pa.).

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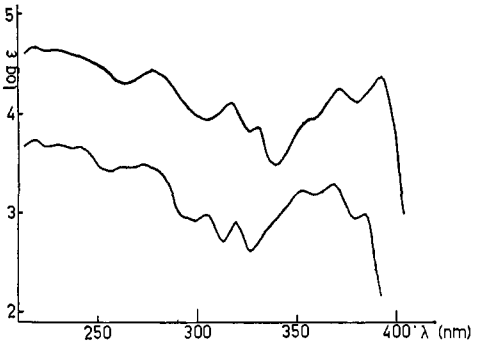

Figure 1. Uv spectra (cyclohexane) of IV and VIII. The spectrum of IV has been shifted downward over 1 log unit for the sake of clearness.

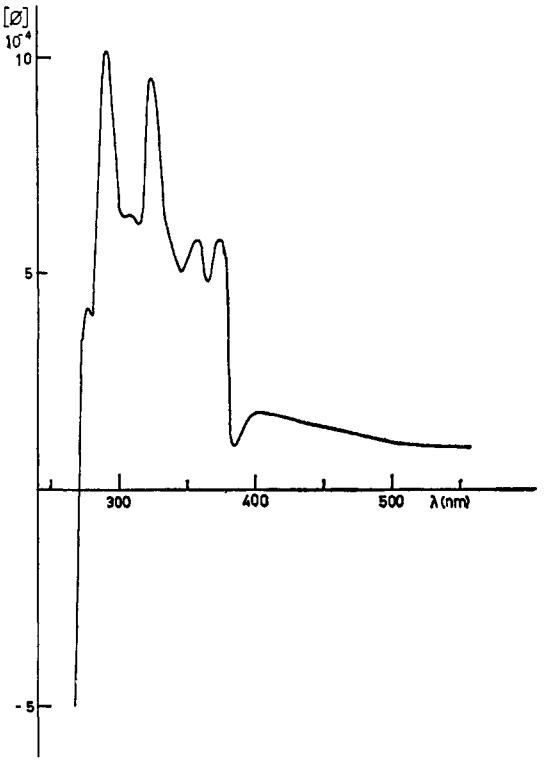

Figure 2. ORD spectrum of IV.

Synthesis, Resolution, and Optical Rotatory Dispersion of a Hexa- and a Heptaheterohelicene

Sir:

Ever since Newman's synthesis and resolution of hexahelicene,[1] the optical properties of this system have fascinated chemists. As the archetype[2] of the inherently dissymmetric chromophore, its large rotation ([ϕ]D 12,200°) coupled with its molecular simplicity ($C_{26}H_{16}$) has given fruitful stimulus to theoreticians.[3] Its laborious synthesis[1,2,4] coupled with a unique but difficult resolution has limited extensive study of this fascinating ring system. The facile synthesis and high yield photocyclization of dithienylethenes to benzo[1,2-*b*:4,3-*b*']dithiophenes[5] prompted us to attempt the preparation of some heterohelicenes.[6] The hexaheterohelicene, benzo[*d*]naphtho[1,2-*d*']benzo[1,2-*b*:-4,3-*b*']dithiophene (IV), and heptaheterohelicene, naphtho[1,2-*d*]benzo[*b*'']thieno[4,5-*d*']benzo[1,2-*b*:4,3-*b*']-dithiophene (VIII), were prepared as shown in Scheme I. The synthesis of the two heterohelicenes proceeded in good yield and deserves little comment.[7] Cyclization to IV was effected in 70% yield by irradiation of a

(1) (a) M. S. Newman, W. B. Lutz, and D. Lednicer, *J. Am. Chem. Soc.*, 77, 3420 (1955); (b) M. S. Newman and D. Lednicer, *ibid.*, 78, 4765 (1956).
(2) J. H. Brewster in "Topics in Stereochemistry," N. L. Allinger and E. Eliel, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967, p 40.
(3) (a) D. D. Fitts and J. G. Kirkwood, *J. Am. Chem. Soc.*, 77, 4940 (1955); (b) A. Moscowitz, *Tetrahedron*, **13**, 48 (1961); (c) I. Tinoco and R. W. Woody, *J, Chem. Phys.*, **40**, 160 (1964).
(4) M. S. Newman, R. S. Darlak, and L. Tsai, *J. Am. Chem. Soc.*, **89**, 6191 (1967).
(5) R. M. Kellogg, M. B. Groen, and H. Wynberg, *J. Org. Chem.*, **32**, 3093 (1967).
(6) Similar ring closures furnishing *benzo*helicenes have recently been described: (a) M. Flammang-Barbieux, J. Nasielski, and R. H. Martin, *Tetrahedron Letters*, 743 (1967); (b) R. H. Martin, M. Flammang-Barbieux, J. P. Cosyn, and M. Gelbcke, *ibid.*, 3507 (1968).
(7) Correct analyses were obtained for all new compounds.