the nature of the D-pentoses attached to position 8 in III or the configuration of their blocking groups at C-2'.

8,5'-Anhydronucleosides of type V are useful intermediates for the synthesis of purine nucleosides of the β -D configuration. Thus, oxidation of Va with an equivalent amount of N-bromosuccinimide in aqueous solution afforded the corresponding sulfoxide (VII, monohydrate) in 67 % yield (Anal. Found: C, 38.41; H, 3.90; N, 22.01; S, 10.07): uv $\lambda_{max}^{H_{2}0}$ 262 nm; $\lambda_{max}^{pH \ 1}$ 265 nm; ir 1040 and 1080 cm⁻¹ (sulfoxide); R_f in solvent A,⁷ 0.29. Treatment of VII (80 mg) with benzoic anhydride9 at 80° for 10 hr and then at 100° for another 10 hr afforded (after removal of benzoic acid and the excess anhydride with ether) VIII (85 mg; 45% yield; λ_{max}^{EcOH} 299, 227 nm; absorbance ratio at two maxima, 1:5.5; homogeneous in tlc; R_f 0.3810). The product VIII (80 mg) was treated with methanolic ammonia at room temperature and subsequently treated with Raney nickel, affording 9- β -Dxylofuranosyladenine (IX, 14 mg, 62% yield). This sample was indistinguishable from an authentic sample prepared by a reported method¹¹ on the criteria of melting point, uv, and R_f in two solvent systems (viz. R_f 0.45 in solvent A,⁷ cf. R_f of VI in the same solvent system, 0.58). Since reaction conditions of each step were not optimized, the overall yield of IX must be improved.

A logical extension of the present work would be a preparation of 2'-deoxyadenosine, which is now in progress in our laboratories.

(9) Pummerer rearrangement: R. Pummerer, Chem. Ber., 43, 1401 (1910).

(10) Silica gel, solvent CHCl₃-EtOH (70:5, v/v).

(11) W. W. Lee, A. P. Martinez, G. L. Tong, and L. Goodman, Chem. Ind. (London), 2007 (1963).

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Structural Consequences of 2,8 Bridging of the Semibullvalene Nucleus¹

Sir:

Historically, semibullvalene can be regarded as the molecule which, because of its unique structural and geometric features, approaches most closely the realization of homoaromatic² cyclic delocalization (of six electrons) in a neutral species. However, a ring current is not observed³ and the semibullvalene transition state appears to reside some 2.3-3.6 kcal/mol in potential energy above the well-known classical structures.⁴ Both EH and MINDO/2 calculations have demonstrated that the placement of substituents on 1 will result in pronounced imbalances of the ground-state equilibrium; 4a, b, 5

(1) Part X of the series entitled Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. For paper IX, see L. A. Paquette and L. M. Leichter, J. Amer. Chem. Soc., 94, 3653 (1972).

(2) S. Winstein, Chem. Soc., Spec. Publ., No. 21, 5 (1969).
(3) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, J. Amer. Chem. Soc., 91, 3316 (1969). (4) (a) M. J. S. Dewar and W. W. Schoeller, *ibid.*, 93, 1481 (1971);

(b) M. J. S. Dewar and D. H. Lo, *ibid.*, **93**, 7201 (1971); (c) F. A. L. Anet and G. E. Schenk, *Tetrahedron Lett.*, 4237 (1970).

(5) R. Hoffmann and W.-D. Stohrer, J. Amer. Chem. Soc., 93, 6941 (1971).

on this basis, annelation of the semibullvalene nucleus with a saturated polymethylene chain at positions 2 and 8 is expected to affect the position of equilibrium only by inductive stabilization and to favor 1a, provided that the "belt" is sufficiently "loose." On the other hand, if the length of the bridge is sufficiently short, isomer 1b



should be overwhelmingly favored in order to bypass the destabilization of **1a** arising from Bredt's rule violations. From the electronic viewpoint, similar bridging with a 1,3-butadienyl moiety could provide a molecule where the actual stable form could instead be the rigid pentaene 2a, or one of the mesovalent Hückellike species 2b (six electron) or 2c (ten electron). If



either of the latter structures were to result, reduction of the activation energy of the Cope rearrangement to a negative value⁵ would be realized experimentally for the first time.

In design, the synthetic scheme is based upon the efficient preparation of semibullvalene realized earlier in this laboratory,⁶ and proceeds by initial elaboration of the annelated 1,8-bishomocubanes 5a and 5b. [4.3.2]Propella-2,4,10-triene (3a)⁷ readily underwent



Diels-Alder reaction with N-phenyltriazolinedione at -70° to give 4a, mp 253.5°.7 That the cycloaddition had occurred virtually exclusively by underside attack⁸ was established by acetone-sensitized photocyclization of 4a to cubyl isomer 5a, mp $204.5^{\circ,7}$ in 92% yield.

⁽⁶⁾ L. A. Paquette, ibid., 92, 5765 (1970); see also R. Askani, Tetrahedron Lett., 3349 (1970).

⁽⁷⁾ Satisfactory analyses (combustion and mass spectrometric) have been obtained for all compounds described herein except 2 and 7 for which only accurate mass determinations are available. In both cases, air sensitivity precluded combustion analysis. In every instance, spectral data supported the structural assignments indicated.

⁽⁸⁾ L. A. Paquette and G. L. Thompson, J. Amer. Chem. Soc., in press.



Figure 1. The 100-MHz nmr spectrum of 7 in CD Cl₃ at 500-Hz sweep width.



Figure 2. The 100-MHz nmr spectrum of 9 in CDCl₃ at 500-Hz sweep width.



Figure 3. The 100-MHz nmr spectrum of 2 in $CDCl_3$ at 500-Hz sweep width.

This cubyl compound underwent smooth Ag⁺-catalyzed isomerization (AgClO₄, anhydrous C₆H₆, reflux, 108 hr) to **6a**, mp 170.5°,⁷ in 86% yield. Hydrolysis of **6a** and subsequent loss of nitrogen were successfully realized

by initial saponification with 86.6% KOH in isopropyl alcohol (100°, 1 hr) under anaerobic conditions, acidification to pH 2 with 3 N HCl (5 min, 0°), readjustment to pH 8 with 3 N NH₄OH, and ultimate oxidation with

activated manganese dioxide. The annelated semibullvalene so obtained (7, calcd m/e 144.0939, found m/e 144.0941, 20% yield) was observed to undergo polymerization when exposed to the atmosphere at ambient temperature for several hours. Confirmation of structure was achieved by catalytic hydrogenation to 8, which was identical with an authentic sample.⁹ On the basis of its electronic properties [$\lambda_{max}^{iscoctane}$ 240 nm (sh) (ϵ 4600)], 7 possesses a typical semibullvalene chromophore. The nmr spectrum (Figure 1) is characterized by a 2:2:2:4:2 ratio of protons, the chemical shifts of which correspond closely to those of semibullvalene^{3,6} and several of its monosubstituted derivatives.¹⁰ We therefore conclude that the equilibrium in the case of 7 (the nmr spectrum remains invariant from -91 to $+116^{\circ}$) is not weighted very heavily in that direction in which the cyclopropane ring occupies a position central to the two larger rings, but consists rather of a near equitable distribution of isomers 7a and 7b.



[4.4.2]Propella-2,4,8,11-tetraene (3b),⁷ readily available by suitable chemical modification⁸ of the corresponding 3,8,11-triene,¹¹ also undergoes ready conversion to 4b, mp 255° (75%).⁷ ($_{\pi}2 + _{\pi}2$) photocyclization of the cyclobutene and bicyclo[2.2.2]octene double bonds in 4b can be affected conveniently by triplet-sensitized (acetone) irradiation. Skeletal rearrangement of 5b7 to dicyclopropyl isomer **6b** was accomplished in 89%yield by heating with a 20-fold molar excess of anhydrous 0.2 N silver perchlorate in benzene for 60 hr in the dark. An additional double bond was introduced into the cyclohexene ring of **6b** by a brominationdehydrobromination sequence which utilized elemental bromine in CH_2Cl_2 at -78° and 1,5-diazabicyclo-[5.4.0]undec-5-ene (DBU) in dry THF at room temperature, respectively.

Hydrolysis of **6b** and **10** was brought about through the agency of potassium hydroxide in aqueous ethylene glycol according to predescribed procedures,⁶ and mild oxidation of the resulting hydrazo compounds was achieved by aeration. Again, diazo decomposition occurred rapidly via the retro-homo Diels-Alder pathway⁶ to give 9 $(37\%)^7$ and 2 $(23\%)^7$ respectively. To allow for ready comparison, the nmr spectra of these polyunsaturated hydrocarbons are illustrated in Figures 2 and 3. In the case of 9, the three groups of olefinic protons and the bridgehead hydrogens appear at chemical shifts in agreement with dominance of the triene tautomer 9 ($\sim 65\%$). In contrast, the spectrum of 2 points clearly to the absence of cyclopropyl character. Not only are the eight peripheral protons decidely olefinic and substantially downfield shifted relative to 9, but H_b is shifted 0.9 ppm upfield while H_a appears 0.6 ppm to lower field. These data, in conjunction with the electronic spectrum $[\lambda_{max}^{isooctane} 239]$ (ϵ 21,000) and 335 nm (1800)], could be construed as

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We are deeply grateful to Professor Rapoport for his generosity in making the authentic sample available to us.
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(11) L. A. Paquette, J. C. Philips, and R. E. Wingard, Jr., J. Amer. Chem. Soc., 93, 4516 (1971).

evidence for the presence of a diamagnetic ring current as in 2c,¹² the shifting of the bridgehead protons then arising from their relative positions in the shielding cone and beyond the rim of the "aromatic" ring, respectively. However, this conclusion must be tempered by the similarity of the nmr spectrum of 2 with that of bicyclo-[5.4.1]dodeca-2,5,7,9,11-pentaene,^{12b} an apparently nondelocalized entity. The extent of the contribution of structures 2b and 2c to the ground state of the pentaene remains consequently a subject for continued study. It is to be particularly noted that should 2 possess some degree of homoaromatic character, overlap of the orbitals at C4 and C6 would be required to be intermediate between σ and π , an unusually important 1,3 interaction which has previously been recognized in an impressive array of *charged* homoaromatic systems^{2,11} but which has evaded customary physical and chemical scrutiny in an uncharged milieu because of the lack of a suitable neutral molecule.

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Crystal and Molecular Structure of [14]Annulene

Sir:

The annulenes have served as suitable objects for the interpretation of nmr spectra¹ and the testing of various theories of π bonding in cyclic conjugated systems.² A detailed knowledge of the molecular structures for the annulenes is invaluable in assessing both spectral measurements and theories.³ According to Hückel's rule, [14]annulene, first synthesized by Sondheimer and Gaoni,⁶ should be aromatic and most probably a planar molecule. It has been shown⁷⁻⁹ that [14]annulene in solution exists as two species, each of which undergoes fast isodynamical transformations at room temperature. Oth has demonstrated recently⁹ that these two species are different configurations, I and II. A two-dimensional X-ray study¹⁰ on [14]annulene indicated that the

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