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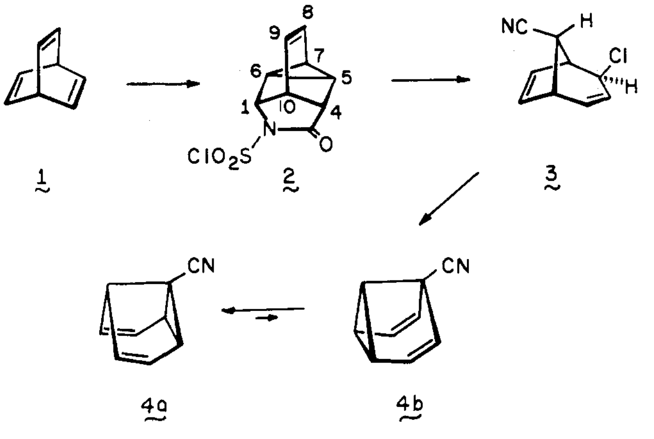
1(5)-Cyanosemibullvalene from Barrelene. Spectral and Crystal Structure Analysis of the Marked Equilibrium Preference Exerted by an Efficient π-Electron Acceptor Substituent

Sir:

Despite the recent development of a variety of synthetic routes to the semibullvalene nucleus,[1-6] the most versatile of these[4,5] still fails in its ability to direct the introduction of such groups as cyano and carbalkoxy. Consequently, the effect of efficient π-electron acceptor substituents on the facile Cope rearrangement process[7] remained to be assessed. In a particularly stringent test of predicted[8] strong equilibrium influences, a highly serviceable route to 1(5)-cyanosemibullvalene has been devised, and the detailed structural features of this molecule have been elucidated. In agreement with theory, the impact of the cyano functionality is to shift the Cope equilibrium toward that direction in which bonding to the cyclopropane ring is heavily preferred. Since a single 7-cyano substituent does not suffice to perturb the cycloheptatriene equilibrium in the norcaradiene direction[9] (two are necessary),[10,11] the structural features peculiar to the semibullvalene nucleus are seen to respond most dramatically to electronic imbalances.

In design, the synthetic scheme is founded upon skeletal reorganization and concomitant suitable functionalization of barrelene (**1**)[12] and proceeds initially by uniparticulate electrophilic addition[13] of chlorosulfonyl isocyanate in dichloromethane solution. Mixing of equimolar quantities of the two reagents at −78° followed by gradual warming during 1 hr to room temperature led in 74% yield to an oily product consisting chiefly of *N*-chlorosulfonyl lactam **2**.[14,15] This material was not purified but treated directly with dimethylformamide at 75-95° for 40 hr.[16] Isolation of the resulting product by preparative VPC at 130° (10% SE-30) afforded *exo*-4-chloro-*anti*-8-cyanobicyclo[3.2.1]octa-2,6-diene (**3**) as a colorless solid, mp 70-71° (31%). Structural assignment to **3** follows from its elemental composition, an intense infrared band (in CH_2Cl_2) at 2245 cm^{-1}, and the ^1H NMR spectrum.[17] As with many dibenzobicyclo[3.2.1]octadienes,[18] the low level of spin interaction between H_4 and H_5 (3 Hz) as well as between the pair of bridgehead protons (H_1,H_5) and H_8 (<1 Hz) uniquely defines the stereochemical features. Treatment of **3** with potassium *tert*-butoxide in DMSO-THF gave **4** in 56% isolated (VPC) yield as colorless white needles, mp 50.5-51°. Quantitative assessment of the **4a** ⇄ **4b** equilibrium constant was not possible on the basis of its ^1H NMR behavior. Although **4a** was clearly indicated to be the predominant isomer, the absence of spectral alteration from 0 to −115° (in CD_2Cl_2-CF_2Cl_2) and the small changes witnessed in the 0 to +99° range ($Cl_2C{=}CCl_2$ solution) were not conducive to measurement of K_{eq}.[5] An estimate was possible by ^{13}C NMR spectroscopy,[19] given the assumption that Anet's value for the chemical shift of C_4 and C_6 (131.8 ppm) in "frozen" semibullvalene recorded at −160° [7c] is relatable to the same carbon atoms in **4a** (130.0 ppm).[20] Using these data, a $K_{eq}{}^{25°}$ of 1.05×10^{-2} results, which translates into an energy difference of 2.8 kcal/mol or 0.12 eV favoring **4a**.



1 **2** **3** **4a** **4b**

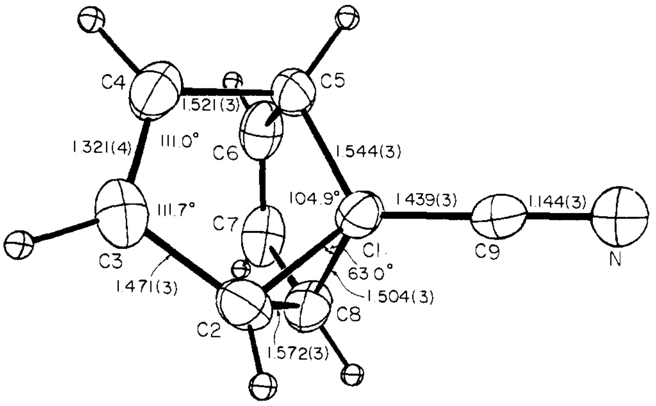


Figure 1.

Full characterization of **4** in the solid state at −45° has been achieved by three-dimensional X-ray crystallographic techniques. As a consequence of the relative stabilities of **4a** and **4b**, the crystals consist wholly of tautomer **4a**. The substance crystallizes with the orthorhombic space group $P2_12_12_1$, with four molecules per cell. The cell constants are: a = 6.693 (2), b = 8.301 (3), and c = 12.393 (4) Å. The phase problem was solved by direct methods using the program MULTAN[21] and the structure refined by the usual methods. After refinement of all the atomic parameters including those of the hydrogen atoms, the R factor is 0.056 for 1192 independent reflections.[22]

The molecule, with bond distances and angles of interest, is illustrated in Figure 1. As shown in Figure 2, the structure possesses nearly exact noncrystallographic mirror symmetry, with the mirror containing C(9), C(1), and C(5) and bisecting the cyclopropane ring. Bonds C(3)-C(4) and C(6)-C(7) are highly localized and characteristically olefinic. The distances between C(4) and C(6) [2.352 (3) Å] and C(3) and C(7) [3.072 (3) Å] are too long for bonding interaction and quite possibly can be no shorter because of repulsive interactions between the opposed π orbitals. The two five-membered rings are significantly nonplanar, with C(3)-C(4) and C(6)-C(7) being forced outward from the planes of the other three atoms in each ring. The angle between the two planes formed by C(2)-C(3)-C(4)-C(5) and C(5)-C(6)-C(7)-C(8) is 98.1°, placing the p-π lobes of

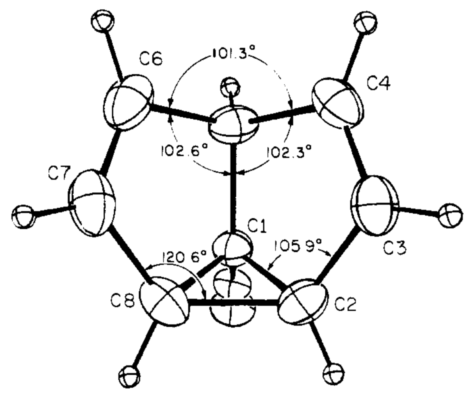


Figure 2.

C(4) and C(6) at approximately right angles to one another. A direct comparison of these data with the structural features of semibullvalene in the gas phase as determined by electron-diffraction methods[23] is informative. Further exploration of this chemistry as a method for introducing more varied substituents is in progress.[24]

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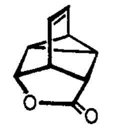
(14) ^{1}H NMR (CDCl$_3$) δ 6.54 (m, $J_{7,8} = 6$, $J_{8,9} = 8$ Hz, H$_8$), 5.80 (t of d, $J_{9,10} = 8$, $J_{7,9} = 2$ Hz, H$_9$), 4.78 (m, $J_{1,6} = J_{1,10} = 2$ Hz, H$_1$), 3.22 (br d, H$_{10}$), 3.03 (br s, H$_4$), 2.53 (tr of d, $J_{5,7} = J_{6,7} = 5.5$ Hz, H$_7$), and 1.85–2.38 (overlapping t, H$_5$ and H$_6$); ν_{max} (CHCl$_3$) 1722 cm^{-1}.

(15) Reductive dechlorosulfonylation of this mixture affords in addition to the parent lactam derived from **2**, lactone i of related structure and the 2 + 2 cycloadduct ii in minor amounts.



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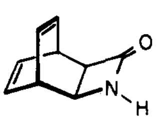

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(17) ^{1}H NMR (CDCl$_3$) δ 6.64 (q, $J_{1,7} = 3$, $J_{6,7} = 5.5$ Hz, H$_7$), 6.26 (m, $J_{1,2} = 6$, $J_{2,3} = 9.5$, $J_{2,4} = 2$ Hz, H$_2$), 5.93 (q, $J_{5,6} = 3$ Hz, H$_6$), 5.43 (m, $J_{3,4} = 2$, $J_{3,5} = 1$ Hz, H$_3$), 4.41 (m, $J_{4,5} = 3$ Hz, H$_4$), 3.38 (s, H$_8$), 3.32 (m, H$_5$), and 3.10 (m, H$_1$).

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(19) ^{13}C NMR (90 MHz, CDCl$_3$, 33°) 130.0 (C$_4$,C$_6$), 119.2 (C$_3$,C$_7$), 56.0 (C$_5$), 49.9 (C$_2$,C$_8$), and 43.3 (C$_1$). Compare also E. Wenkert, E. W. Hagaman, L. A. Paquette, R. E. Wingard, Jr., and R. K. Russell, *J. Chem. Soc., Chem. Commun.*, 135 (1973).

(20) Solvent and inductive effects have necessarily been disregarded. However, because the cyano function is positioned δ to C$_4$,C$_8$, through-bond effects are expected to be minimal. The Hoffmann–Stohrer prediction has **4a** stabilized by 0.37 eV.[8]

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(24) We acknowledge partial support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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A New Synthesis of Sucrose Which Demonstrates a Novel Approach to the Synthesis of α-Linked Disaccharides[1]

Sir:

In spite of recent advances[2] in the field, stereochemically controlled preparation of α-linked disaccharides remains one of the most challenging frontiers in synthetic organic chemistry.[3] Among compounds linked in this manner are some of the most important biologically, pharmacologically, and clinically active substances, and frequently the structural features of the individual saccharide components vary widely.[4] We describe herein a novel approach to the synthesis of α-linked disaccharides which is capable of accomodating a wide variety of structural modifications, and, as a case in point, we illustrate this potential by outlining a synthesis of sucrose[5] from known starting materials.

Specifically, (i) the disaccharide linkage is forged by the agency of an electrophile, a novel development which might be availing where current nucleophilic–solvolytic type condensations[2,7] are inapplicable; (ii) the glucosyl moiety is elaborated from an hex-2-enopyranoside, a type of unsaturated sugars of demonstrated versatility in monosaccharide modification;[8,9] (iii) congeners of some of the intermediates, e.g., **16** have provided access to 2-amino-2-deoxydisaccharides of pharmacological importance;[10] (iv) the linkage of the fructosyl unit via a tertiary alcohol (actually a tertiary ketol) occurs in 45% yield; (v) all steps in the synthesis occur under mild conditions and are so stereo- or regiospecific that no chromatographic fractionations are necessary, excepting that following the initial condensation.

The key to the synthesis reported here is diene **3**,[11] prepared most expeditiously by elimination of methanol from **2**,[12] the latter being obtained from ketone **1**.[13] Diene **3** has been shown to undergo methoxybromination to the α-glycoside **6a**,[14] a result which may be rationalized in terms of the extensively delocalized allyloxocarbonium ion, **4**, resulting from electrophilic attack on **3** (Scheme I). Ion **4** is expected to capture the nucleophile preferentially on the α-face since the product so formed (**6a**) allows for better continuous overlap with the intermediate than does the alternative β-product (**5a**). Interestingly, in analogy with the "axial haloketone" principle,[15] compound **6a** would not only be the kinetic product but is thermodynamically favored because of the Edward–Lemieux effect.[16]

The foregoing advantage, based on an electronic assessment, is complemented by an equally favorable stereochemical prognosis. Thus intermediate **4**, because of its planar foreground, presents no steric obstacles to the approaching nucleophile.

Condensation of diene **3** and tetraacetylfructofuranose **7** under the agency of iodonium ion[17] afforded compound **6b**