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Chlorocyanation of Barrelenes as a Route to 1-Cyanosemibullvalenes. Convenient Introduction of an Efficient π-Electron Acceptor Substituent and Its Influence on the Cope Equilibrium

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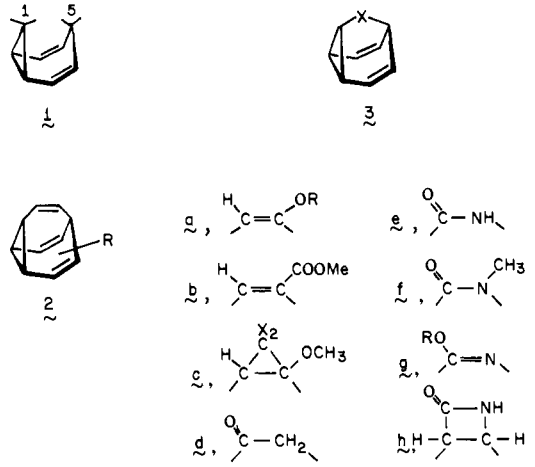
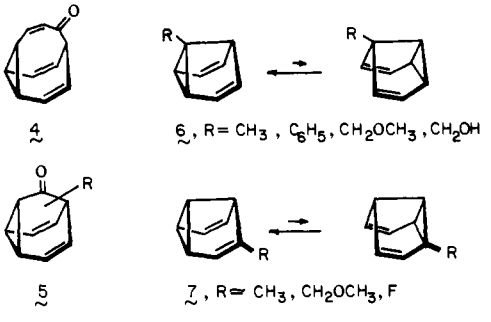
Abstract: The two-step sequence of chlorosulfonyl isocyanate addition to a barrelene followed by heating in a dimethylformamide at ca. 90° proceeds with skeletal rearrangement to a [3.2.1] bicyclic frame and introduction of cyano and chloro substituents in a 1,3 relationship. These products undergo ready dehydrohalogenation with potassium *tert*-butoxide in Me_2SO–THF solution at room temperature to give 1-cyanosemibullvalenes. By NMR and x-ray methods, the parent nitrile is shown to exist in that tautomeric form having the CN substituent bonded to the cyclopropane ring at C_1. The mono- and dibenzo analogues lack the capability for Cope rearrangement and are consequently locked into this form as well. The initially formed barrelene–CSI adducts have been characterized and certain mechanistic conclusions drawn. The structural parameters of 1(5)-cyanosemibullvalene are discussed in light of known cyclopropane bond lengths and those features peculiar to the semibullvalene derivative are summarized.

As a consequence of their fluxional character, unsymmetrically bridged homotropilidenes (**1**) can satisfy internal electronic requirements by shifting the position of structural equilibrium. Although Schröder's investigation[1] of monosubstituted bullvalenes (**2**) has indicated that such weakly



accepting and donating groups as methyl, chloro, bromo, and iodo discriminate hardly at all between the various available sites, fluorobullvalene exists chiefly (80–85%) in that form where the electronegative functionality prefers the lone sp^3-hybridized aliphatic carbon (C-5). With alkoxy and carbomethoxy substituents, the preferred orientation is that illustrated in **3a–c**.[1,2] Therefore, at the bullvalene level of homologation, a general pattern of preferential equilibration in the C-5 direction is seen. When an electron-withdrawing carbonyl group is introduced as in bullvalone (**3d**)[3] or the lactams **3e**[4] and **3f**,[5] the result is to alter the prevailing competition chiefly in the opposite direction, and this trend is maintained in the azabullvalenes **3g**[6] and β-lactam **3h**.[7]

Goldstein's more recent finding[2] that homobullvalenone **4** is characterized by preferred bonding of the carbonyl terminus to C-5 conflicts with those trends found in the lower homologues and is not easily reconciled with available theoretical assessments of electronic effects in Cope equilibria.[8,9] Because complications from larger longicyclic frameworks[10] can arise from a number of sources, the true electronic perturbational effects in **4** are conceivably not being revealed. This is not so



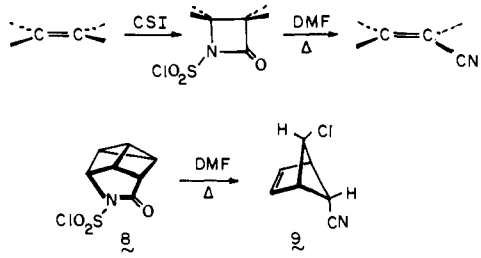
in the twofold degenerate barbaralone series (**5**) where methyl is recognized to prefer C-1 (K = 3.28) and deuterium C-5 (K = 0.80).[11] In those 1(5)- and 2(4)-substituted semibullvalenes (**6** and **7**, respectively) examined to date,[12b,c] the equilibria are clearly illustrative of preferential attachment to olefinic > cyclopropyl > aliphatic, irrespective of the particular substituent. With the exception of **7**-F, good agreement is found with prediction.[8,9] However, the effect of an efficient π-electron acceptor such as cyano on the very facile[13] Cope rearrangement process which operates in semibullvalenes remained to be assessed.

The choice of cyano for the present investigation was predicted upon the following considerations. Thermochemical studies have indicated the effects of nitrile groups on strained ring stability to be minor.[14] Such combustion measurements deal, however, with total stabilizing effects and do not consider specific bond weakening and strengthening influences which may be operating within the molecule.[11] That individual cyclopropane ring bonds are affected by such forces is suggested by the appreciable shift in the cycloheptatriene–norcaradiene equilibrium witnessed in the case of the 7-cyano derivative.[15,16] Unlike the semibullvalene valence isomerization process, this last equilibrium is not degenerate, lies too far to one side in the parent system, and consequently is difficult to assess quantitatively.

Because the currently available access routes to nonaryl fused semibullvalenes[12,17-20] are not conducive to introduction of a cyano substituent, a new route to this class of compounds was developed, the details of which are now presented. We also report herein on the structural features of the simplest derivative.[21]

Synthetic Aspects

As a consequence of the pioneering work of Graf and his coworkers,[22] it is now feasible to convert a simple alkene to an α,β-unsaturated nitrile through solvolysis in dimethylformamide solution of its chlorosulfonyl isocyanate (CSI) adduct. Moriconi and Jalandoni have addressed the mechanism of these *N*-(chlorosulfonyl) β-lactam ring-opening reactions and shown the process to be general.[23] Where a comparably N-substituted γ-lactam is concerned, the action of dimethylformamide at elevated temperatures results instead in conversion to a γ-chloro nitrile. The transformation of **8** into **9** is illustrative.[24]

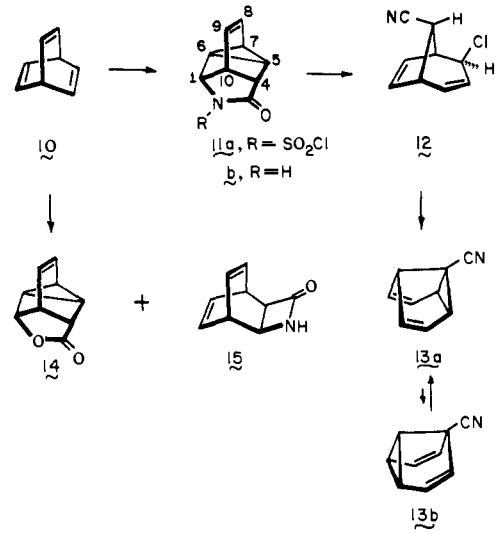


8 9

Lactams of general structure **8** are known to result on occasion from CSI additions to polyolefinic or strained hydrocarbons prone to structural isomerization under electrophilic conditions. Because the barrelene nucleus contains the requisite eight carbon atoms and is recognized to be predisposed toward skeletal reorganization,[25] our synthetic plan was founded on the anticipation that a γ-chloro nitrile resembling **9** would result and be capable of further 1,3-elimination of HCl with cyclopropane ring formation. These goals have been realized.

Barrelene. Mixing of equimolar quantities of barrelene (**10**)[25] and CSI in dichloromethane solution at −78 °C followed by gradual warming to room temperature led in 74% yield to an oily product consisting chiefly of *N*-(chlorosulfonyl) γ-lactam **11a** (Scheme I). This structural assignment follows mainly from infrared (ν_{max} ($CHCl_3$) 1722 cm^{-1}) and ^1H NMR spectral data ($CDCl_3$ solution). In particular, only two well-separated olefinic C–H signals are present at δ 6.54 (m, $J_{7,8} = 6$, $J_{8,9} = 8$ Hz, H_8) and 5.80 (t of d, $J_{9,10} = 8$, $J_{7,9} = 2$ Hz, H_9). Additionally, those protons flanking the lactam functionality are distinctive [4.78 (m, $J_{1,6} = J_{1,10} = 2$ Hz, H_1) and 3.03 (br s, H_4)], while the three cyclopropyl hydrogens appear at 2.53 (t 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). Heating of this unpurified material in dimethylformamide at 75–95° for 40 h and isolation of the resulting product by preparative VPC afforded *exo*-4-chloro-*anti*-8-cyanobicyclo[3.2.1]octa-2,6-diene (**12**) as a colorless solid in 31% yield. The definitive spectral data for **12** include an intense infrared band (in CH_2Cl_2) at 2245 cm^{-1} and a ^1H NMR spectrum which indicates not only that four olefinic protons are present [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), and 5.43 (m, $J_{3,4} = 2$, $J_{3,5} = 1$ Hz, H_3)] but also uniquely defines the stereochemical features at H_4 and H_8. As with many dibenzo[3.2.1]octadienes,[26] the low level of spin interaction between H_4 (4.41, m, $J_{4,5} = 3$ Hz) and H_5 (3.32, m), as well as between the pair of bridgehead protons (H_1, H_5) and H_8 (<1 Hz) is reconcilable only with an exo,anti arrangement of the two substituents. Treatment of **12** with potassium *tert*-butoxide in Me_2SO–THF gave **13** in 56% isolated (VPC) yield. The semibullvalene was obtained as indefinitely stable colorless needles which proved quite amenable to three-dimensional x-ray crystal structure analysis.[21]

Scheme I

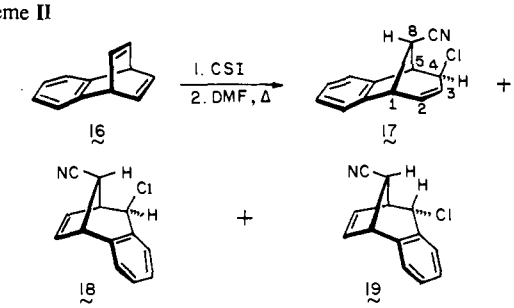


10 11a, R = SO_2Cl; b, R = H 12 14 15 13a 13b

In order to obtain more definitive information on the original CSI adduct mixture, the crude product was hydrolyzed with saturated sodium sulfite and 10% potassium hydroxide solutions.[27] Separation of the components could be achieved most satisfactorily by chromatography on Florisil, but with substantial losses of material.[28] By this technique, three adducts could be obtained in pure form and these were identified as lactone **14**, γ-lactam **11b**, and β-lactam **15**. These assignments of structure accord fully with the derived spectra and receive further support from their close similarity to related adducts isolated from the CSI–homobarrelene cycloaddition.[28]

Benzobarrelene. Under the preestablished conditions, benzobarrelene (**16**)[29] was comparably reactive toward CSI. Direct treatment of the cycloadduct mixture with warm dimethylformamide followed by careful silica gel chromatography led to isolation of three chloronitriles **17–19** in yields of 23.5, 23.8, and 6.5%, respectively (Scheme II). A synopsis of the proton coupling constants exhibited by these closely related benzobicyclo[3.2.1]octadienes is given in Table I. Those

Scheme II



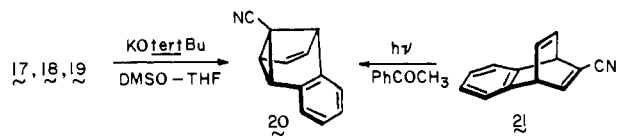
16 17 18 19

Table I. ^{1}H NMR Coupling Constant Data for Chloro Nitriles **17**, **18**, and **19** ($CDCl_3$ Solution, 60 MHz)

Spin interaction, J	Coupling constant, Hz		
	17	**18**	**19**
1,2	6.4		
1,7		2.9	2.8
1,8	4.0	<1	<1
2,3	9.5		
2,4	1.2		
2,8	1.0		
3,4	3.3		
3,5	1.7		
4,5	1.2	2.9	5.1
5,6		2.9	2.5
5,8	4.0	<1	<1
6,7		5.5	5.6

coupling patterns which are important for stereochemical characterization of this triad are $J_{4,5}$, $J_{1,8}$, and $J_{5,8}$. As a direct consequence of the prevailing rigid geometries and the recognized reliability of the Karplus rule[30] in bicyclo[3.2.1]octane systems,[26] the dihedral angle relationships of the C-5–H bond to an endo- (~60°) or exo-4-proton (~40°) and to an anti- (~40°) or syn-8-proton (~80°) are sufficiently distinctive to be revealed by the magnitude of the spin–spin interactions. Thus, the low order of $J_{4,5}$ in **17** and **18** (1.2–2.9 Hz) is uniquely accommodated by an endo-4-proton, whereas the larger coupling constant in **19** (5.1 Hz) connotes an exo orientation for H_4. That **18** and **19** contain a syn-8-proton is indicated by the weak coupling (<1 Hz) to H_5, a phenomenon not shared by **17** (4.0 Hz) whose 8-proton must therefore be anti. The identical values of $J_{1,8}$ prove nicely corroborative.

Upon individual brief treatment of **17–19** with potassium *tert*-butoxide in Me_2SO–THF solvent at room temperature, dehydrohalogenative closure occurred with formation of 1-cyanobenzosemibullvalene (**20**) in each instance. The yields

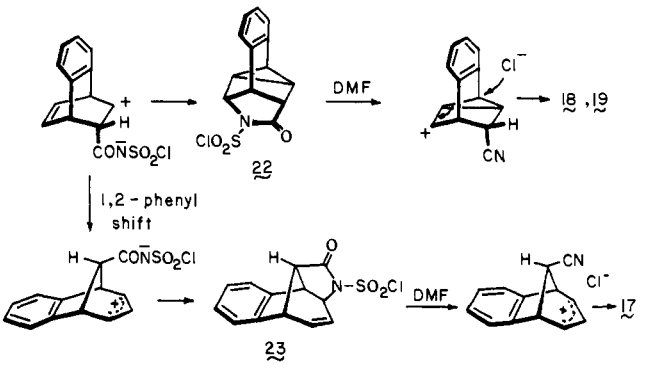


proved quite acceptable (85–88%). In view of the recognized ease of reversible abstraction of C-4 benzylic protons under such alkaline conditions,[31] it is likely that the 4-chloro substituent in **18** is epimerized prior to being displaced. Such a process may also be operative in **17**; however, the stereochemical requirements are not as rigid here, since an S_N2' mechanism having precisely the opposite stereochemical demands to the direct S_N2 pathway[32] can gain importance. This feature is also relevant to the cyclization of **12**.

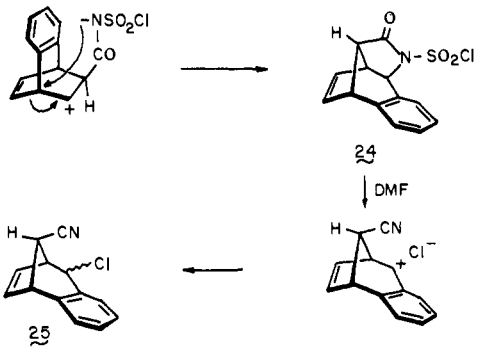
Bender and Shugarman have recently established that **20** can also be obtained exclusively by subjecting 2-cyanobenzobarrelene (**21**) to triplet-sensitized irradiation.[33]

Mechanistically, it is possible that **17**, **18**, and **19** arise by initial CSI attack anti to the benzene ring in benzobarrelene with subsequent electronic reorganization such that **22** and **23** are produced (Scheme III). The action of DMF on this pair of intermediates would result in chlorocyanation via mechanistically plausible channels[23] with **22** ultimately providing **18** and **19**, and **23** giving rise to **17**. In contrast, entry of the electrophile from the syn direction would require a 1,2-vinyl shift before arriving at a γ-lactam intermediate, viz. **24** (Scheme IV). The structural features of **24** would provide for ultimate conversion to epimeric chloro nitriles of formula **25**. Since such compounds are not components of the product

Scheme III

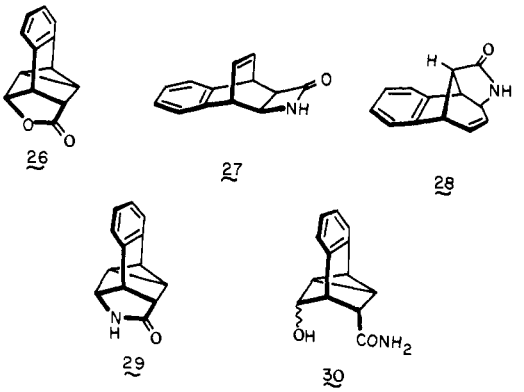


Scheme IV



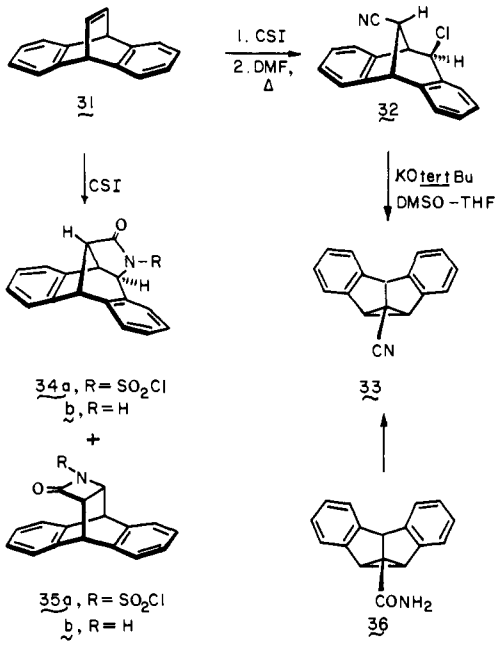
mixtures, it becomes highly likely that electrophilic capture from the syn direction is kinetically unfavorable. This is not to say that **25** was not present in very small amounts and remained undetected.

The results obtained when the CSI reaction mixture was hydrolyzed directly are also consistent with stereoselective capture. Careful chromatography of the crude hydrolysate led to the isolation of lactone **26**, lactams **27–29**, and hydroxy amide **30**, the obvious hydrolysis product of **29**. These structural assignments are fully supported by ir and ^{1}H NMR data, detailed analysis of which is provided in the Experimental Section. It is particularly relevant that no γ-lactam corresponding to **24** was detected.



Dibenzobarrelene. Lastly, the reactivity of **31** toward CSI merits reporting. When equimolar amounts of these two substances were heated at the reflux temperature of dichloromethane for 70 h (note diminished reaction rate) and the resulting product mixture treated directly with dimethylformamide, chloronitrile **32** could be isolated in low yield after silica gel chromatography (Scheme V). The exo-4 and anti-8 stereochemistry of **32** follows primarily from the low order of spin–spin interaction between H_4 and H_5 (2.2 Hz) as well as between H_8 and the two bridgehead protons (~1 Hz).[31] The presence of a rearranged [3.2.1] bicyclic skeleton in **32** is fully consistent with its facile base-promoted cyclization to diben-

Scheme V



zocyanosemibullvalene (**33**), an authentic sample of which was prepared from known carboxamide **36**[34] by conventional methods. The independent synthesis of **33** gains importance because this particular cyanosemibullvalene lacks all but three of the ring protons which so uniquely characterize the ^{1}H NMR spectra of the less substituted analogs **13** and **20.**

Chromatographic (silica gel) purification of the reaction mixture produced upon treatment of **31** with CSI furnished 2.7% of **32** together with principal adduct **34a** and lesser quantities (2.2%) of the *N*-(chlorosulfonyl) β-lactam **35a.** Seemingly, **32** results from partial degradation of **34a** during this workup, a phenomenon not lacking precedent.[35] The obtention of **35a** is of interest because ionic additions to **31** generally proceed[36] with carbon skeleton rearrangement to give 4,8-disubstituted dibenzobicyclo[3.2.1]octadienes in both nonpolar[37] and polar[38] solvents. The possibility exists that **35a** is the result of concerted 2 + 2 cycloaddition. Of perhaps greater significance is the fact that **35a** does not undergo isomerization to **34a** under the reaction conditions. When a mixture of **35a** and **34a** (2:3) was heated in CH_2Cl_2 at the reflux temperature for 140 h, no increase in the amount of **34a** could be noted although some decomposition of **35a** was evident. This intrinsic unreactivity of **35a** is without question the factor which permits its isolation. Reductive dechlorosulfonylation of this pair of adducts was effected as before to give **34b** and **35b**, the spectral properties of which were also consistent with the respective formulations.

^{1}H and ^{13}C NMR Spectra

Tables II and III contain typical low- and high-temperature 100-MHz ^{1}H NMR data for **13a** ⇄ **13b** in two different solvent systems. In CD_2Cl_2–CF_2Cl_2, the small amount of $CDHCl_2$ present served as an internal standard for monitoring changes in chemical shift as a function of ΔT. Two sets of downfield signals are seen, each with a relative area of 2, and these exhibit negligible variable-temperature dependence. Since the $H_{3,7}$ and bridgehead (H_5) protons are likewise not appreciably affected either in the low-temperature range or between 0 and 100°, these data do not permit determination of K_{eq} as has been possible with other semibullvalenes,[12,39] although clear indication is provided that **13a** is heavily dominant.

An estimate of this most important parameter is made possible by ^{13}C NMR spectroscopy. The ^{13}C spectrum of semibullvalene at room temperature is characterized by three resonances at 50.0 (C-1,5), 86.5 (C-2,4,6,8), and 120.4 ppm (C-3,7).[40] At −160 °C, where the Cope rearrangement becomes "frozen out", five signals appear at 42.2, 48.0, 53.1, 121.7, and 131.8 ppm assignable to C-2,8, C-1, C-5, C-3,7, and C-4,6, respectively.[13] The ^{13}C results for **13** determined at room temperature in the present study indicate a comparable five-line series of resonances at 43.3 (C-1), 49.9 (C-2,4), 56.0 (C-5), 119.2 (C-3,7), and 130.0 ppm (C-4,6). Expectedly, the inductive influence of the nitrile substituent exerts a shielding effect at C-1 while deshielding C-2,8. Because of their proximity to CN, these carbons are not directly relatable to those of the parent hydrocarbon. However, the permanently olefinic carbons (C-3,7) show a quite close correspondence in the two systems (121.7 vs. 119.2), presumably as a consequence of their more remote position relative to the cyano group. Given the assumption that C-4,6 would also be little effected, the chemical shift of these carbons in "frozen" semibullvalene (131.8 ppm) should be directly relatable to that of the same carbons in **13a** (130.0 ppm). Using these values, a $K_{eq}^{25°}$ of 2.05×10^{-2} is calculated, which translates into an energy difference of 2.4 kcal/mol or 0.10 eV favoring **13a.** Hoffmann and Stohrer[8] previously calculated the energy difference between **13a** and **13b** to be 8.5 kcal/mol or 0.37 eV in favor of the 1-isomer. The equilibrium constant demanded by these calculations is 5.8×10^{-7} at 25°.

The ^{13}C spectra of **20** and **33** have been recorded for comparison purposes (see Experimental Section).

X-Ray Crystal Structure Analysis. To more accurately assess the structural question, at least as it relates to the solid state, Beno and Christoph[21,41] have subjected **13** to three-dimensional x-ray crystallographic analysis at −45°. Under these conditions, the crystals were found to consist wholly of tautomer **13a.** Two illustrations of the structure have appeared previously,[21] and consequently only the more significant molecular dimensions (cf. **37**) shall be commented upon here. Direct comparison of the bond lengths in **13a** with the structural features of semibullvalene as determined by electron diffraction in the gas phase (see **38**)[42] and of the 7,7-dicyanonorcaradiene[39] (x-ray methods)[16] is particularly informative. For example, while the C-1–C-5 bridge in **38** is a short

Table II. Variable-Temperature ^{1}H NMR Chemical Shifts (100 MHz) for 1(5)-Cyanosemibullvalene in CD_2Cl_2–CF_2Cl_2 (δ units)

Temp, °C	$CDHCl_2$	$H_{2,8}$	$H_{3,7}$	$H_{4,6}$	H_5
−1	5.30	3.45	5.21	5.75	3.51
−17	5.31	3.46	5.21	5.77	3.53
−31	5.32	3.48	5.22	5.78	3.56
−50	5.34	3.47	5.23	5.81	3.56
−75	5.36	3.48	5.24	5.83	3.58
−95	5.38	3.50	5.26	5.85	3.60
−115	5.40	3.53	5.27	5.87	3.64

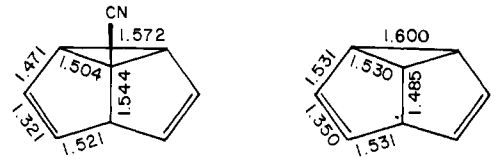
Table III. Variable-Temperature ^{1}H NMR Chemical Shifts (100 MHz) for 1(5)-Cyanosemibullvalene in $Cl_2C{=}CCl_2$ (δ units)

Temp, °C	$H_{2,8}$	$H_{3,7}$	$H_{4,8}$	H_5
−19	3.38	5.15	5.69	3.46
−4	3.38	5.15	5.67	3.45
19	3.39	5.15	5.64	3.44
32	3.41	5.14	5.63	3.43
49	3.41	5.14	5.60	3.43
60	3.42	5.14	5.58	3.41
72	3.43	5.14	5.57	3.42
84	3.43	5.14	5.55	3.41
99	3.46	5.14	5.53	3.41

Table IV. Bond Lengths in Cyclopropane Derivatives

Compound	Method[a]	Remote internal bond, Å	Proximal or edge bond, Å	Ref
Cyclopropane	MW	1.510		*b*
Chlorocyclopropane	MW	1.515	1.513	*c*
1,1-Dichlorocyclopropane	MW	1.534	1.532	*d*
Cyclopropane-1,1-dicarboxylic acid	X	1.462	1.534	*e*
Bicyclopropyl	X (−100°)	1.487	1.501	*f*
Cyclopropanecarboxamide	X	1.481	1.507	*g*
Cyclopropanecarbohydrazide	X	1.48	1.50	*h*
cis-1,2,3-Tricyanocyclopropane	X	1.518		*i*
Bicyclo[1.1.0]butane	MW	1.497	1.498	*j*
Bicyclo[2.1.0]pentane	ED	1.439	1.521	*k*
exo,anti-Tricyclo[3.1.1.0^{2,4}]heptan-6-yl *p*-nitrobenzoate	X	1.54	1.48	*l*
8,8-Dichlorotricyclo[3.2.1.0^{1,5}]octane	X (−40°)	1.572	1.458	*m*
2,5-Dimethyl-7,7-dicyanonorcaradiene	X	1.501	1.556	*n*
Semibullvalene	ED	1.600	1.530	*o*
syn-8,8-Dichloro-4-phenyl-3,5-dioxabicyclo[5.1.0]octane	X	1.53	1.48	*p*
Axivalin hydrate	X	1.51	1.49	*q*
6,6-Diphenyl-3-3-diethyl-3-azabicyclo[3.1.0]hexane	X	1.525	1.517	*r*
anti-8-Tricyclo[3.2.1.0^{2,4}]octyl *p*-bromobenzenesulfonate	X	1.54	1.51	*s*
Benzocyclopropapyran	X	1.51	1.52	*t*
trans-Bicyclo[5.1.0]octane-4-carboxylic acid	X	1.31	1.49	*u*
trans-Bicyclo[5.1.0]octane-4-methanol *p*-bromobenzenesulfonate	X	1.20	1.41	*u*
Potassium *trans*-bicyclo[5.1.0]octane-4-carboxylate	X	1.464	1.509	*v*
cis-Bicyclo[5.1.0]octane-4-*exo*-*p*-bromobenzenesulfonate	X	1.499	1.500	*u*

[a] MW = microwave spectroscopy; X = x-ray diffraction; ED = electron diffraction. [b] O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964). [c] R. H. Schwendeman, G. D. Jacobs, and T. M. Kriggs, *J. Chem. Phys.*, **40**, 1022 (1964). [d] W. H. Flygare, A. Narath, and W. D. Gwinn, *ibid.*, **36**, 200 (1962). [e] M. A. M. Meester, H. Schenk, and C. H. Mac Gillavry, *Acta Crystallogr. Sect. B*, **27**, 630 (1971). [f] J. Eraker and C. Romming, *Acta Chem. Scand.*, **21**, 2721 (1967); see also O. Bastiansen and A. de Meijere, *ibid.*, **20**, 516 (1966). [g] R. E. Long, H. Maddox, and K. N. Trueblood, *Acta Crystalogr. Sect. B*, **25**, 2083 (1969). [h] D. B. Chestnut and R. E. Marsh, *Acta Crystallogr.*, **11**, 413 (1958). [i] A. Hartman and F. L. Hirshfield, *ibid.*, **20**, 80 (1966). [j] K. W. Cox and M. D. Harmony, *J. Chem. Phys.*, **50**, 1976 (1969). [k] R. K. Bohn and Y. H. Tai, *J. Am. Chem. Soc.*, **92**, 6447 (1970). [l] S. Masamune, R. Vukov, M. J. Bennett, and J. T. Purdham, *J. Am. Chem. Soc.*, **94**, 8239 (1972). [m] K. B. Wiberg, G. J. Burgmaier, K. Shen, S. J. LaPlaca, W. C. Hamilton, and M. D. Newton, *ibid.*, **94**, 7402 (1972). [n] Reference 16. [o] Reference 42. [p] G. R. Clark and G. J. Palenik, *J. Chem. Soc., Perkin Trans. 2*, 194 (1973). [q] G. D. Anderson, R. S. McEwen, and W. Hertz, *Acta Crystallogr. Sect. B*, **29**, 2783 (1973). [r] F. R. Ahmed and E. R. Gabe, *Acta Crystallogr.*, **17**, 603 (1964). [s] A. C. MacDonald and J. Trotter, *ibid.*, **18**, 243 (1965). [t] L. G. Guggenberger and R. A. Jacobson, *Acta Crystallogr. Sect. B*, **25**, 888 (1969). [u] R. A. Kershaw, Ph.D. Thesis, The Ohio State University, 1974. [v] R. A. Kershaw, M.S. Thesis, The Ohio State University, 1972.



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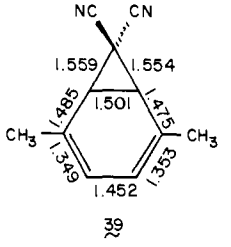

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single bond at 1.485 Å, the 1-cyano substituent has the effect of returning this bond to the more normal length of 1.544 Å. Wang and Bauer recognized the labile C-2–C-8 bond in semibullvalene to be of abnormally large dimension (1.600 Å). Because the cyano group can constantly maintain a π-interactive conformation relative to the cyclopropane ring, the expectation follows[8] that strengthening of the C-2–C-8 linkage should result. In actuality, a reduction in length of approximately 0.03 Å is seen, but the value of 1.572 Å remains appreciably larger than that of 1.501 Å seen for **39**. Although **39** is geminally substituted by two nitrile groups and their combined influence will serve to shorten the opposite cyclopropane σ bond the more so, the C-2–C-8 distance in **37** lies well outside the expected range for substituted cyclopropanes (Table IV). In fact, the length is closely akin to that determined for the highly strained central bond in the small-ring propellane, 8,8-dichlorotricyclo[3.2.1.0^{1,5}]octane (Table IV).

This structural feature which is innate to the semibullvalene nucleus reflects itself in rather dramatic responses to electronic imbalances. Thus, the impact of a lone cyano substituent at C-1 is to shift the Cope equilibrium heavily to that direction in which cyclopropyl bonding prevails. By comparison, one 7-cyano group does not suffice to perturb the cycloheptatriene equilibrium in the norcaradiene direction.[15b] Two such groups are necessary to achieve this end result.[15a]

The two five-membered rings in **37** were found to be significantly nonplanar with C-4 and C-6 being forced in an outwardly direction. The net effect of this distortion is to orient the two pπ orbitals in an approximately orthogonal relationship such that some repulsive interaction is generated. The resultant C-4–C-6 distance (2.352 Å) is clearly too large for bonding interaction, although it is understandably shorter than that between the more remote C-3–C-7 pair (3.072 Å).

As is usual, the relationship between the x-ray structure and the dynamic situation in solution is not necessarily directly correlative, since the real possibility exists that crystal packing forces might perturb the energetics. Notwithstanding, it is now clear that the cyano function exerts a most profound ground-state influence favoring cyclopropyl bonding over attachment to trigonal carbon in complete agreement with extended Hückel theory.

Experimental Section

Infrared spectra were recorded on Perkin-Elmer Model 137 and 467 spectrometers, whereas mass spectra were obtained with an AEI-MS9 instrument at an ionizing potential of 70 eV. Proton magnetic resonance spectra were obtained using Varian A-60A and HA-100 spectrometers. Apparent splittings are given in all cases. ^{13}C NMR data were acquired on a Bruker HX-90 spectrometer. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***N*-(Chlorosulfonyl)-2-aza-3-oxoquadricyclo[4.4.0.0^{4,10}.0^{5,7}]dec-8-ene (11a).** A magnetically stirred solution of 610 mg (5.86 mmol) of barrelene (**10**)[25] in 15 ml of dry dichloromethane cooled to −78° was treated dropwise with a solution of chlorosulfonyl isocyanate (830 mg, 5.86 mmol) in 10 ml of the same solvent. After 7 h at −78°, the temperature was allowed to return slowly to 20° overnight. Upon cooling to −10°, the mixture was diluted with ether (10 ml) followed by 25 ml of saturated sodium sulfite and 2 ml of 10% potassium hydroxide solutions (rapid stirring). The pH was adjusted to 8 with 5% hydrochloric acid, and stirring was continued at room temperature for 10 min. The layers were separated, the aqueous phase was extracted with ether (50 ml), and the combined organic solutions were washed with 50-ml portions of 5% HCl, saturated $NaHCO_3$, and brine solutions prior to drying and evaporation. The residual pale yellow oil (995 mg, 74%) was now comprised chiefly of **11a**, ν_{max} ($CHCl_3$) 1722 cm^{-1}. ^1H NMR data are provided in the text.

***exo*-4-Chloro-*anti*-8-cyanobicyclo[3.2.1]octa-2,6-diene (12).** A solution of **10** (30 mg, 0.29 mmol) in 2 ml of dry dichloromethane cooled to −78° was treated with 41 mg (0.29 mmol) of CSI while stirred magnetically. The temperature of the solution was allowed to warm gradually to room temperature and maintained there for 1 h. Dimethylformamide (3 ml) was introduced, and after 3 h the dichloromethane was removed by fractional distillation (pot temp 80 °C). The clear brown solution was heated at 75–95 °C for 40 h and poured into 10 ml of cold water. The aqueous layer was diluted with 5 ml of saturated $NaHCO_3$ solution and extracted with ether (20 ml). The residue obtained after drying and evaporation of the combined organic layers was purified by preparative VPC on 10% SE-30 at 130° (0.25 in. × 6 ft column). There was collected 15 mg (31%) of **12** as a colorless oil which crystallized upon sublimation at 50 °C and 25 mm, mp 70–71 °C; ν_{max} (CH_2Cl_2) 2245 cm^{-1}. The ^1H NMR data are provided in the text.

Anal. Calcd for C_9H_8ClN: C, 65.27; H, 4.87. Found: C, 64.91; H, 4.99.

1(5)-Cyanosemibullvalene (13). A magnetically stirred solution of freshly purified **12** (50 mg, 0.30 mmol) in 5 ml of anhydrous tetrahydrofuran cooled to −5° under nitrogen was treated dropwise with a solution of freshly sublimed potassium *tert*-butoxide in 3.5 ml of dry dimethyl sulfoxide. After completion of the addition, the solution was allowed to warm to 20° where it was stirred for 20 min before being poured into pentane (50 ml) and water (20 ml). The layers were separated and the aqueous phase was reextracted with pentane (2 × 30 ml). The combined pentane fractions were washed with water (20 ml), dried, and concentrated by fractional distillation. The concentrate was subjected to preparative VPC on a silanized 5% SE-30 column (0.25 in. × 2 ft) through which triethylamine had been passed earlier (70°). The only component was isolated to give 22 mg (55%) of **13**; ν_{max} (CH_2Cl_2) 2233 cm^{-1}; δ_{Me_4Si}(CD_2Cl_2-CF_2Cl_2) 5.75 (d of m, $J_{3,4}$ = $J_{6,7}$ = 5.3 Hz, $J_{4,5}$ = $J_{5,6}$ = 2.2 Hz, $J_{2,4}$ = $J_{6,8}$ = 1.2 Hz, 2 H, H_4 and H_6), 5.21 (d of t, $J_{2,3}$ = $J_{7,8}$ = 1.4 Hz, $J_{3,5}$ = $J_{5,7}$ = 0.4 Hz, 2 H, H_3 and H_7), 3.51 (br t, 1 H, H_5), and 3.45 (m, 2 H, H_2 and H_8); δ_{Me_4Si}(CS_2) 5.65 (m, 2 H, H_4 and H_6), 5.17 (m, 2 H, H_3 and H_7), 3.35–3.48 (m, 3 H, H_2, H_5, and H_8); λ_{max} (C_2H_5OH) intense end absorption only; *m/e* (calcd) 129.0578, (found) 129.0580.

Addition of CSI to 10 and Subsequent Hydrolysis. An 800-mg sample (7.7 mmol) of **10** was treated with 1.13 g (8.0 mmol) of chlorosulfonyl isocyanate as above. After 1 h at 20°, the reaction mixture was cooled to 0°, diluted with ether (25 ml), and treated with freshly prepared saturated sodium sulfite solution (50 ml) and ether (25 ml). After a pH adjustment to 8, the emulsion was stirred for 1 h at 0° and the layers were separated. The aqueous layer was extracted with dichloromethane (2 × 100 ml) and the combined organic layers were washed with water (100 ml) and saturated ammonium chloride solution (50 ml). Drying and evaporation left a yellow solid which was subjected to chromatography on Florisil. Elution with ether–pentane (4:1) afforded 37 mg (3.1%) of 2-oxa-3-oxoquadricyclo[4.4.0.0^{4,10}.0^{5,7}]dec-8-ene (**14**) which was sublimed (60 °C and 50 mm) and recrystallized from hexane. The fine white needles had mp 61–62 °C; ν_{max} ($CHCl_3$) 1778 cm^{-1}; δ_{Me_4Si}($CDCl_3$) 6.37 (m, $J_{7,8}$ = 6 Hz, $J_{8,9}$ = 8 Hz, 1 H, H_8), 5.70 (t of m, $J_{9,10}$ = 7 Hz, 1 H, H_9), 4.23 (t, $J_{1,6}$ = $J_{1,10}$ = 2.5 Hz, 1 H, H_1), 3.06 (d of m, 1 H, H_{10}), 2.33 (m, 1 H, H_7), 2.23 (m, 1 H, H_{10}), 2.01 (t of m, $J_{5,8} \approx J_{6,7}$ = 6 Hz, 1 H, H_6), and 1.84 (t of m, $J_{5,7}$ = 6 Hz, 1 H, H_5); *m/e* (calcd) 148.0526, (found) 148.0528.

Anal. Calcd for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 73.19; H, 5.65.

Elution with increasing proportions of ethyl acetate in ether gave 60 mg (4.9%) of a mixture of **11b** and **15** rich in the first lactam: δ_{Me_4Si} ($CDCl_3$) 6.47 (m, 1 H, H_8), 5.89 (m, 1 H, H_9), 5.75 (br s, 1 H, >NH), 3.59 (m, 1, >CH-N<), 2.63–2.90 (m, 2 H, >CHCO- and H_{10}), and 1.6–2.5 (m, 3 H, cyclopropyl).

Sublimation of the lactam mixture (70 °C and 30 mm) caused selective destruction of **11b** and furnished 8 mg (0.7%) of 3-aza-4-oxotricyclo[4.2.2.0^{2,5}]deca-7,9-diene (**15**) as off-white prisms, mp 152.5–154 °C (from ether–hexane): ν_{max} ($CHCl_3$) 1751 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.12–6.52 (m, 4 H, olefinic), 5.80 (br s, 1, >NH), 3.88–4.22 (m, 2 H, bridgeheads), 3.80 (t of d, $J_{1,2}$ = $J_{2,5}$ = 4.5 Hz, $J_{2,x}$ = 1 Hz, 1 H, >CHN<), and 3.54 (t of d, $J_{5,6}$ = 4.5 Hz, $J_{5,y}$ = 1.5 Hz, 1 H, >CHCO-); *m/e* (calcd) 147.0684, (found) 147.0687.

Chlorocyanation of Benzobarrelene (16). Chlorosulfonyl isocyanate (2.83 g, 20.0 mmol) dissolved in 10 ml of dry dichloromethane was added dropwise during 20 min to a magnetically stirred solution of **16** (3.00 g, 19.5 mmol)[29] in 45 ml of the same solvent at room temperature under argon. After 18 h, 1 ml of dimethylformamide was added and the dichloromethane removed by distillation while an additional 30 ml of dimethylformamide was introduced. When the internal temperature reached 80°, distillation was discontinued. The reaction mixture was heated at 80° for 50 h, cooled, and poured into 300 ml of ice water. Workup in the predescribed fashion afforded 3.21 g (74.4%) of a mixture of chloro nitriles.

This oil was chromatographed on silica gel (150 g) using hexane elution containing 1–20% ether. The first component isolated was identified as **18** (1.00 g, 23.8%), thick needles, mp 147.5–148.5 °C (from ether–hexane); ν_{max} ($CHCl_3$) 2250 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.83–7.50 (m, 4 H, aryl), 6.54 (q, $J_{6,7}$ = 5.5 Hz, $J_{1,7}$ = 2.9 Hz, 1 H, H_7), 5.87 (q, $J_{5,6}$ = 2.9 Hz, 1 H, H_6), 4.99 (d, $J_{4,5}$ = 2.9 Hz, 1 H, H_4), 3.71 (d, 1 H, H_1), 3.54 (s, 1 H, >CHCN), and 3.49 (t of m, 1 H, H_5); *m/e* (calcd) 215.0502, (found) 215.0504.

Anal. Calcd for $C_{13}H_{10}ClN$: C, 72.39; H, 4.67; N, 6.49. Found: C, 72.25; H, 4.75; N, 6.18.

The second component (0.988 g, 23.5%) proved to be **19.** A pure sample of this chloro nitrile was obtained by recrystallization from ether–hexane and sublimation (90 °C and 0.02 mm) as a colorless crystalline solid, mp 140.5–141.5 °C; ν_{max} ($CHCl_3$) 2250 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.83–7.65 (m, 4 H, aryl), 6.48 (dd, $J_{6,7}$ = 5.6 Hz, $J_{1,7}$ = 2.8 Hz, 1 H, H_7), 5.99 (dd, $J_{5,6}$ = 2.5 Hz, 1 H, H_6), 5.24 (d, $J_{4,5}$ = 5.1 Hz, 1 H, H_4), 3.53–3.80 (m, 2 H, H_1 and H_5), and 3.05 (s, 1 H, H_8); *m/e* (calcd) 215.0502, (found) 215.0504.

Anal. Calcd for $C_{13}H_{10}ClN$: C, 72.39; H, 4.67; N, 6.49. Found: C, 72.43; H, 4.69; N, 6.25.

Lastly, 274 mg (6.5%) of **17** was isolated, white needle clusters, mp 109–111 °C (from ether–hexane); ν_{max} ($CHCl_3$) 2247 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.05–7.53 (m, 4 H, aryl), 6.35 (q of t, $J_{2,3}$ = 9.5 Hz, $J_{1,2}$ = 6.4 Hz, $J_{2,4}$ = 1.2 Hz, $J_{2,8}$ = 1.0 Hz, 1 H, H_2), 5.58 (d of q, $J_{3,4}$ = 3.3 Hz, $J_{3,5}$ = 1.7 Hz, 1 H, H_3), 4.47 (m, $J_{4,5}$ = 1.2 Hz, 1 H, H_4), 3.62–4.00 (m, 2 H, H_1 and H_5), and 3.46 (t of d, $J_{1,8}$ = $J_{5,8}$ = 4.0 Hz, 1 H, H_8); *m/e* (calcd) 215.0502, (found) 215.0504.

Anal. Calcd for $C_{13}H_{10}ClN$: C, 72.39; H, 4.67; N, 6.49. Found: C, 72.61; H, 4.52; N, 6.67.

1-Cyanobenzosemibullvalene (20). A. Cyclization of 18. A solution of 200 mg (1.78 mmol) of sublimed potassium *tert*-butoxide in 2 ml of dry dimethyl sulfoxide was added in one portion to a magnetically stirred solution of **18** (200 mg, 0.927 mmol) in 3 ml of dry dimethyl sulfoxide and 3 ml of anhydrous tetrahydrofuran under argon at room temperature. After 10 min, the solution was poured into a mixture of ether (50 ml) and ice water (100 ml). The layers were separated and the aqueous phase was extracted with ether (50 ml) and dichloromethane (50 ml). The combined organic layers were washed with water (2 × 30 ml), dried, and evaporated to leave a pale yellow oil which was subjected to silica gel chromatography. Elution with 5% ether in hexane furnished 147 mg (88%) of **20**, mp 94–95 °C (from ether–hexane) (lit.[33] mp 95–96 °C); ν_{max} ($CHCl_3$) 2232 cm^{-1}; δ_{Me_4Si}

($CHCl_3$) 6.95-7.45 (m, 4 H, aryl), 5.67 (q of m, $J_{5,6}$ = 2.4 Hz, $J_{6,7}$ = 5.3 Hz, 1 H, H_6), 5.14 (q, $J_{7,8}$ = 2.4 Hz, 1 H, H_7), 4.16 (d, 1 H, H_5), 3.65 (d, $J_{2,8}$ = 7.3 Hz, 1 H, H_2), and 3.28 (q of d, $J_{x,8}$ = 0.6 Hz, 1 H, H_8); ^{13}C NMR ($CDCl_3$) 148.0, 134.0, 136.4, 127.0, 126.8, 125.4, 121.1, 119.0, 118.9, 56.6, 45.9, 44.2, and 43.1 ppm; *m/e* (calcd) 179.0735, (found) 179.0739.

B. Cyclization of 19. A 200-mg (0.927 mmol) sample of **19** was treated with potassium *tert*-butoxide (200 mg, 1.78 mmol) as described above. Chromatography of the crude product on silica gel afforded 145 mg (87%) of **20**, mp 94-95 °C.

C. Cyclization of 17. From 27 mg of **17** and 27 mg of KO-*tert*-Bu, there was obtained after chromatography 19 mg (85%) of **20**, mp 94-95 °C.

Addition of CSI to 16 and Subsequent Hydrolysis. A magnetically stirred solution of **16** (1.00 g, 6.48 mmol) in 10 ml of dry dichloromethane cooled to 0° under nitrogen was treated dropwise during 30 min with a solution of freshly distilled chlorosulfonyl isocyanate (920 mg, 6.50 mmol) in 10 ml of the same solvent. Reaction was allowed to proceed for 24 h at room temperature before removal of solvent under vacuum. The residual yellow oil was dissolved in ether (15 ml) and added to a rapidly stirred mixture of ether (10 ml) and 25% aqueous sodium sulfite solution (15 ml) at 0°. During this addition, the pH was maintained at 7-8 with small amounts of 10% potassium hydroxide. This mixture was maintained at 0° for 30 min at room temperature for an equal length of time. The ether layer was separated and the aqueous phase extracted with ether (2 × 50 ml). The combined organic layers were dried and evaporated to give a pale yellow solid, the analysis of which showed it to be a fairly complex mixture.

A 1.57-g sample of such a mixture was carefully chromatographed on silica gel. Elution with hexane-ethyl acetate (4:1) afforded lactone **26** (130 mg), mp 146.5-147 °C (from ether-hexane); ν_{max} ($CHCl_3$) 1780 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.03-7.50 (m, 4 H, aryl), 4.47 (m, 1, H_1), 3.49 (m, 1 H, H_{10}), 2.79 (d of d, $J_{5,7}$ = 6.4 Hz, $J_{6,7}$ = 7.0 Hz, 1 H, H_7), 2.43 (m, 1 H, H_4), and 1.80-2.37 (m, 2 H, $H_{5,6}$).

Anal. Calcd for $C_{13}H_{11}O_2$: C, 78.77; H, 5.09. Found: C, 78.53; H, 5.11.

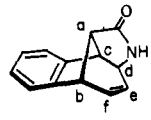
Gradual increase in solvent polarity to 80% ethyl acetate in hexane led to isolation of β-lactam **27** (219 mg), mp 198.5-199.5 °C (from dichloromethane-ether); ν_{max} ($CHCl_3$) 1755 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.91-7.33 (m, 4 H, aryl), 6.18-6.72 (m, 2 H, olefinic), 3.90-4.24 (m, 2 H, benzylic), 3.48-3.71 (m, 1 H, >CH-N<), and 3.16-3.40 (m, 1 H, >CHCO-).

Anal. Calcd for $C_{13}H_{11}NO$: C, 79.17; H, 5.62; N, 7.10. Found: C, 78.86; H, 5.61; N, 7.13.

$Eu(fod)_3$ pseudocontact shifting of the NMR spectrum gave the following ΔEu values: H_1, −2.0; H_2, −3.6; >NH, −7.6; H_5, −9.9; H_6, −6.7; H_7, −4.3; H_8, −1.8; H_{9-11}, −1.2; and H_{12}, −2.2.

With ethyl acetate as eluent, there was obtained a mixture of the above β-lactam (360 mg) and γ-lactam **28** (297 mg, percentage composition derived from ^1H NMR integration). The latter component was isolated in pure form by repeated recrystallization from dichloromethane-ether as colorless crystals, mp 191-191.5 °C; ν_{max} ($CHCl_3$) 1707 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.93-7.43 (m, 4 H, aryl), 6.70 (br s, 1 H, >NH), 5.98-6.33 (m, 1 H, olefinic), 5.50-5.81 (q of m, 1 H, olefinic), 3.92-4.20 (m, 1 H, >CHCO-), 3.66-3.92 (m, 1 H, >CH-N<), and 3.21-3.60 (m, 2 H, benzylic).

Double resonance studies provided the following coupling constants:[43] $J_{c,e}$ = 1.4 Hz; $J_{c,d}$ = 3.0 Hz; $J_{a,c}$ = 2 Hz; $J_{b,f}$ = 6.0 Hz; $J_{b,e}$ = 1.4 Hz; $J_{a,b}$ = 4.5 Hz; $J_{e,f}$ = 9.2 Hz; $J_{d,f}$ = 1 Hz; $J_{a,f}$ = 0.7 Hz; $J_{d,e}$ = 4.5 Hz; $J_{c,f}$ = 0.8 Hz; $J_{a,d}$ = 1 Hz.



Anal. Calcd for $C_{13}H_{11}NO$: C, 79.17; H, 5.62; N, 7.10. Found: C, 78.88; H, 5.59; N, 7.20.

Two additional products were admixed in the fractions immediately following (dichloromethane-ethyl acetate elution). Recrystallization from dichloromethane-ether gave pure hydroxy amide **30** as colorless needles, mp 149-149.5 °C; ν_{max} ($CHCl_3$) 3300, 3190, and 1669 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.86-7.28 (m, 4 H, aryl), 6.13 (br s, 2 H, $-NH_2$), 5.39 (br s, 1 H, OH), 3.56 (m, 1 H, >CHO-), 3.11 (m, 1 H, bridgehead), and 1.68-2.45 (m, >CHCO- and cyclopropyl).

Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.15; H, 6.12; N, 6.50.

The mother liquors from above were evaporated and the residue crystallized from ether. Physical separation of the solid rosettes (due to lactam **29**) from the needle clusters of **30** and recrystallization of the first material from dichloromethane provided pure **29**, mp 210-210.5 °C; ν_{max} ($CHCl_3$) 1669 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.00-7.48 (m, 4 H, aryl), 6.82 (br s, 1 H, >NH), 3.20-3.43 (m, 2 H, >CH-N< and bridgehead), 2.77 (apparent t, J = 6.7 Hz, 1 H, benzylic cyclopropyl), 2.18-2.33 (m, 1 H, >CHCO-), and 1.78-2.35 (m, 2 H, cyclopropyl).

Anal. Calcd for $C_{13}H_{11}NO$: C, 79.17; H, 5.61; N, 7.10. Found: C, 78.80; H, 5.75; N, 7.05.

2,3;6,7-Dibenzo-*exo*-4-chloro-*anti*-8-cyanobicyclo[3.2.1]octa-2,-6-diene (32). A solution of 400 mg (1.95 mmol) of **31**[44] in 5 ml of dry dichloromethane was treated with 310 mg (2.19 mmol) of CSI while stirred magnetically under argon. After 70 h at the reflux temperature, the yellow solution was diluted with 5 ml of dimethylformamide and the majority of the dichloromethane was removed by distillation. Upon heating the residual liquid at 80° for 50 h under argon, a clear brown solution was obtained. This was poured into ice water and the product was extracted with ether (2 × 50 ml) and dichloromethane (50 ml). The combined organic phases were washed with water and saturated sodium bicarbonate solution before drying and evaporation. There remained 530 mg of a yellowish semisolid which was chromatographed on silica gel (35 g). Elution with 7% ether in hexane afforded 45 mg (10% based on recovered **31**) of **32**, pale yellow crystals, mp 185.5-186.6 °C (from dichloromethane-ether); ν_{max} ($CHCl_3$) 2246 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.87-7.46 (m, 8 H, aryl), 5.12 (d, $J_{4,5}$ = 2.2 Hz, 1 H, H_4), 4.22 (narrow m, 1 H, H_1), 4.01 (m, 1 H, H_5), and 3.81 (narrow m, 1 H, H_8); *m/e* (calcd) 265.0658, (found) 265.0663.

Anal. Calcd for $C_{17}H_{12}ClN$: C, 76.84; H, 4.55; N, 5.27. Found: C, 76.61; H, 4.75; N, 5.27.

1-Cyanodibenzosemibullvalene (33). A. 1,3-Elimination from 32. A solution of **32** (40 mg, 0.15 mmol) in dry tetrahydrofuran (1 ml) and anhydrous dimethyl sulfoxide (1 ml) was stirred magnetically under argon while 35 mg (0.31 mmol) of freshly sublimed potassium *tert*-butoxide was introduced. The light-brown reaction mixture was stirred for 10 min at room temperature and worked up as above to give 31 mg (90%) of **33** as white needles, mp 211-212.5 °C (from ether-hexane); ν_{max} ($CHCl_3$) 2238 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.89-7.38 (m, 8 H, aryl), 4.72 (s, 1 H, H_5), and 3.67 (s, 2 H, cyclopropyl); ^{13}C NMR ($CDCl_3$) 149.0 (2 C), 133.9 (2 C), 127.7 (2 C), 127.3 (2 C), 125.2 (2 C), 121.1 (2 C), 57.1, 45.2 (2 C), and 44.4 ppm.

Anal. Calcd for $C_{17}H_{12}N$: C, 88.67; H, 5.25. Found: C, 88.93; H, 4.85.

B. Dehydration of 36. A suspension of 150 mg (0.61 mmol) of **36** in 15 ml of sodium-dried benzene and 180 μl of anhydrous triethylamine was heated with magnetic stirring until dissolution. The heating bath was removed and 180 mg (1.5 mmol) of thionyl chloride was introduced. After 5 h at the reflux temperature, the solution was cooled, diluted with ether (50 ml) and dichloromethane (50 ml), and poured into ice water. The aqueous phase was separated and extracted with ether (50 ml). The combined organic layers were washed with 50-ml aliquots of 5% hydrochloric acid, saturated sodium bicarbonate, and brine solutions prior to drying and evaporation. The crude product (170 mg) was purified by preparative TLC (silica gel; benzene elution) and recrystallization from ether-hexane. There was isolated 55 mg (39%) of **33** as white needles, mp 211-212.5 °C, which proved identical with the material above.

Addition of CSI to 31 and Subsequent Hydrolysis. A solution of 2.247 g (11.0 mmol) of **31** and 1.56 g (11.0 mmol) of freshly distilled CSI in 25 ml of dry dichloromethane was heated at reflux under argon for 72 h while magnetically stirred. After cooling, the solvent was evaporated and the residue was chromatographed on silica gel. Elution with hexane-ethyl acetate (4:1) gave 80 mg (2.7%) of **32**, mp 185.5-186.5 °C, with spectral properties identical with the sample isolated earlier.

Enhancement in solvent polarity to 50% ethyl acetate furnished 730 mg (19.1%) of **34a**, dense white prisms, mp 210-211 °C (from dichloromethane-ether); ν_{max} ($CHCl_3$) 1772 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.82-7.42 (m, 8 H, aryl), 5.37 (dd, $J_{1,7}$ = 5 Hz, $J_{7,10}$ = 3 Hz, 1 H, >CHN<), 4.27 (m, 2 H, benzylic bridgeheads), and 3.78 (t of d, $J_{1,10}$ = $J_{4,10}$ = 5 Hz, 1 H, >CHCO-).

Anal. Calcd for $C_{17}H_{12}ClNO_3S$: C, 59.03; H, 3.50; N, 4.05. Found: C, 58.98; H, 3.63; N, 4.06.

Several early fractions in the latter series contained small amounts of **35a** (estimated 2.2% yield) which resisted purification by fractional crystallization or preparative TLC. The derived β-lactam could in contrast be purified without difficulty (see below).

Dechlorosulfonylation of 34a. A solution of 110 mg (0.318 mmol) of **34a** in 5 ml of dichloromethane and 10 ml of ether was stirred magnetically while 10 ml of 25% sodium sulfite solution and 10 drops of 10% KOH were added. After 4 h, dichloromethane was added to dissolve the solid which formed and stirring was continued for an additional hour. After addition of ether (50 ml) and 5% HCl (100 ml), the organic layer was separated, washed with saturated $NaHCO_3$ and NaCl solutions, dried, and evaporated. Lactam **34b** was obtained in quantitative yield: mp 256.5–257.5 °C (from dichloromethane–ether); ν_{max} ($CHCl_3$) 1710 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.73–7.32 (m, 8 H, aryl), 5.93 (br s, 1 H, >NH), 4.33 (m, 1 H, H_1), 4.18 (m, 2 H, H_4 and H_5), and 3.54 (t of d, 1 H, >CHCO–); *m/e* (calcd) 247.0997, (found) 247.1001.

Dechlorosulfonylation of 35a. A 273-mg sample of a mixture of **35a** and **34a** was treated with sodium sulfite solution as above to give 200 mg (80%) of a mixture of **35b** (three parts) and **34b** (five parts). Repeated recrystallization from dichloromethane–ether removed **35b** and provided ultimately 26 mg of pure β-lactam, mp 246–247 °C dec; ν_{max} ($CHCl_3$) 1758 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.83–7.83 (m, 8 H, aryl), 5.58 (br s, 1 H, >NH), 4.33 (m, 2 H, benzylic bridgeheads), 3.75 (m, 1 H, >CHN<), and 3.42 (t or m, 1 H, >CHCO–); *m/e* (calcd) 247.0997, (found) 247.1001.

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