A Synthetic Entry into the Azasemibullvalene System. Unsaturated Heterocyclic Systems. LXII[1,2]

Leo A. Paquette and Grant R. Krow

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received April 22, 1969*

Abstract: The synthesis of an azasemibullvalene derivative has been accomplished in three steps commencing with the addition of chlorosulfonyl isocyanate to hexamethyl(Dewarbenzene) (**5**). The stereochemistry of electrophilic addition to **5** is discussed. A rearrangement of lactam **11** is described.

The consequence of rigidly locking a divinylcyclopropane moiety into an all-*cis* conformation as, for example, in bullvalene (**1**) and semibullvalene (**2**) is manifested in a marked acceleration of the Cope rearrangement.[3] In azabullvalene derivatives such as **3**, rapidly reversible [3.3]-sigmatropic shifts are also evident; however, the presence of an imino ether function in the bullvalene molecule drastically diminishes the number of accessible structural arrangements from 1,209,600 in **1** to only 28 in **3**.[4] The apparent reasons for this behavior have been discussed.[4a] Although the magnitude of the energy barrier in **3** which prevents the nitrogen atom from entering into Cope rearrangement is not known at the present time, Staab and his coworkers have shown that valence isomerizations requiring the involvement of imino nitrogen do occur at moderate temperatures.[5] These considerations led us to undertake the synthesis of an azasemibullvalene such as **4** in which the elements of a *cis*-fused divinylcyclopropane and an imine function coexist. At issue was the question of whether this ring system would exhibit fluxional character. The present paper describes an exceptionally facile three-step synthesis of a derivative of **4** and provides some insight into the chemical behavior of the azasemibullvalene molecule.[6]


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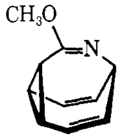

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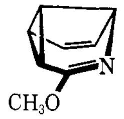

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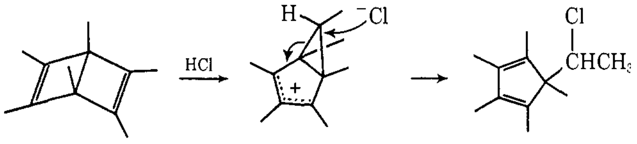
Results. Previously, we reported that exposure of hexamethyl(Dewar benzene) (**5**) to hydrohalogen acids and a variety of related electrophiles results in the formation of α-ethylpentamethylcyclopentadiene derivatives (**7**).[7] To account for the striking, and perhaps unique, fact that these ionic transformations eventuate in bonding of both moieties of the electrophilic reagent to the same carbon atom, the intermediacy of cyclopropylcarbinyl cations such as **6** was invoked. More recent nmr studies on the protonation of **5** in strongly acidic solutions have revealed that rapidly equilibrating bicyclo[2.1.1]hexenyl cations predominate in this medium.[8] Although these latter cations may reside at an energy minimum under these conditions, earlier work[7,9] suggested that a set of isomeric and interconvertible cations may exist on a single energy surface.[10]



5 **6** **7**

With the realization that azasemibullvalene **4** is fundamentally a $(CH)_7N$ species and that **5** is a $(CH)_6$-based hydrocarbon with considerable driving force for the production of a plethora of carbonium ions, a reasonable route to **4** appeared to involve the addition of a potential (CH)N fragment to **5** in the appropriate fashion. The successful utilization of the powerfully electrophilic chlorosulfonyl isocyanate (CSI) reagent in the conversion of cyclooctatetraenes to zwitterionic homotropylium cation intermediates[11] has led to an examination of the CSI–hexamethyl(Dewar benzene) reaction for this purpose. Addition of CSI to **5** in cold (−15°) methylene chloride solution afforded a crystalline N-(chlorosulfonyl) lactam which, without purification, was carefully hydrolyzed in aqueous acetone by titration with 4 *N* sodium hydroxide solution to give the derived amide in 87% over-all yield. An understanding of the mechanistic details of this cycloaddition reaction required elucidation of the structure of the lactam for which five plausible structural formulations can be writ-

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(1) For the previous paper in this series, see L. A. Paquette, G. R. Krow, and J. R. Malpass, *J. Am. Chem. Soc.*, in press.

(2) We are indebted to the National Institutes of Health for their generous support of this work.

(3) For an extensive discussion of this point, see W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(4) (a) L. A. Paquette, J. R. Malpass, G. R. Krow, and T. J. Barton, *J. Am. Chem. Soc.*, **91**, 5296 (1969); (b) L. A. Paquette and T. J. Barton, *ibid.*, **89**, 5480 (1967); (c) L. A. Paquette, T. J. Barton, and E. B. Whipple *ibid.*, **89**, 5481 (1967).

(5) H. A. Staab and F. Vögtle, *Chem. Ber.*, **98**, 2701 (1965), and other papers in this series.

(6) For a preliminary report of a portion of this study, see L. A. Paquette, *Tetrahedron Letters*, 2133 (1968).

(7) L. A. Paquette and G. R. Krow, *ibid.*, 2139 (1968).

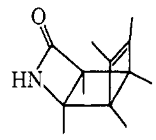
(8) (a) L. A. Paquette, G. R. Krow, J. M. Bollinger, and G. A. Olah, *J. Am. Chem. Soc.*, **90**, 7147 (1968); (b) H. Hogeveen and H. C. Volger, *Rec. Trav. Chim.*, **87**, 385 (1968).

(9) (a) D. M. Lemal and J. P. Lokensgard, *J. Am. Chem. Soc.*, **88**, 5934 (1966); (b) W. Schäfer and H. Hellmann, *Angew. Chem. Intern. Ed. Engl.*, **6**, 518 (1967); (c) H. Hoogeveen and H. C. Volger, *Chem. Commun.*, 1133 (1967); (d) G. M. Atkins, Jr., and E. M. Burgess, *J. Am. Chem. Soc.*, **90**, 4744 (1968); (e) R. Criegee and H. Grüner, *Angew. Chem. Intern. Ed. Engl.*, **7**, 467 (1968).

(10) This set of cations has been illustrated in ref 8a.

(11) (a) L. A. Paquette, J. R. Malpass, and T. J. Barton, *J. Am. Chem. Soc.*, **91**, 4714 (1969); (b) L. A. Paquette and T. J. Barton, *ibid.*, **89**, 5480 (1967).

ten: **8** and its *exo* isomer, **9**, **10**, and **11**. The absence of a β-lactam ring system was revealed by the carbonyl absorption at 1690 cm^{-1}. Further, this amide slowly absorbed hydrogen when reduced catalytically over rhodium on carbon at room temperature to give a *lone* dihydro derivative (**12**), $\nu_{max}^{CHCl_3}$ 1690 cm^{-1}. A similar stereochemical result was observed when the lactam was epoxidized with *m*-chloroperbenzoic acid in chloroform solution to yield a *single* epoxide, ν_{max}^{Nujol} 1700 cm^{-1}. The accumulated data thus establish that the lactam



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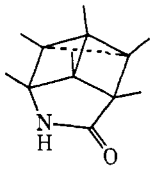

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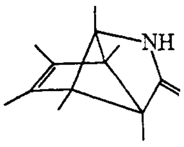

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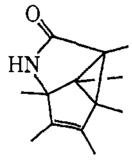
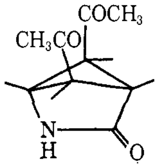


11

possesses a single site of unsaturation and must therefore be tricyclic. At this point, structures **8** and **9** could be dismissed as logical possibilities, and it remained to differentiate between **10** and **11**.



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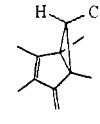
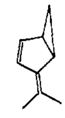
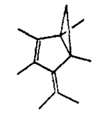
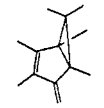
It was recognized that reconciliation of the stereoselective nature of the hydrogenation and oxidation reactions with structure **10** would be difficult, and therefore effort was made to rule out this possibility. On being oxidized with buffered potassium permanganate in acetone solution, the lactam was converted in 65% yield to a crystalline diketone whose nmr spectrum displayed two sharp acetyl methyl singlets at δ 2.28 and 2.07. Because the plane of symmetry in the diketone derivable from **10**, *viz.* **12**, requires that both acetyl groups be magnetically equivalent, formula **10**, or any other symmetrical species, is totally inconsistent with these spectral properties.

Highly compelling evidence for structure **11** was derived from partial Hofmann degradation. Thus, sequential methylation, lithium aluminum hydride reduction, and quaternization of the lactam afforded a highly crystalline methiodide. Pyrolysis of the corresponding methohydroxide gave an unsaturated tertiary amine which was characterized as its perchlorate salt. In particular, the nmr spectrum of this amine displayed the two methylene protons as a collapsed AB doublet at δ 5.01 and 4.92 and its ultraviolet absorption was characteristic of a 2,3-homofulvene chromophore (Table I).

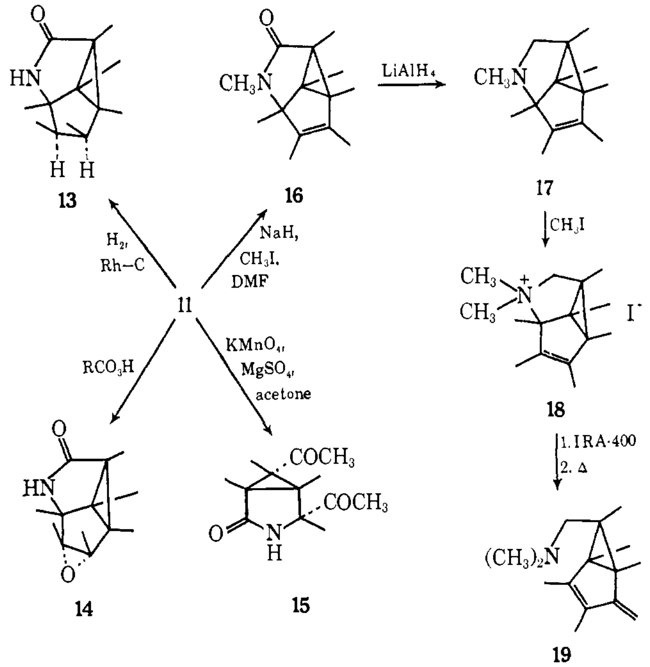
The transformations described above have been summarized in Chart I. The existence of **11** in a rigid cup-like conformation is consistent with the selectivity observed in the formation of **13** and **14**, the particular reagent presumably preferring approach from the less congested *exo* surface. Also, diacetyl derivative **15** exhibits spectral properties in complete accord with the structural assignment (see Experimental Section).

Table I. Ultraviolet Spectra of 2,3-Homofulvenes

Compound	Uv maximum, nm (ϵ)	Ref
19	$\lambda_{max}^{C_2H_5OH}$ 257 (7,540)	This work
	$\lambda_{max}^{CH_3OH}$ 255 (10,600)	*a*
	$\lambda_{max}^{C_2H_5OH}$ 245 (10,900)	*b*
	$\lambda_{max}^{C_2H_5OH}$ 257 (12,780)	*b*
	$\lambda_{max}^{C_2H_5OH}$ 257 (8,940)	*b*
	$\lambda_{max}^{C_2H_5OH}$ 253 (11,300)	*c*

[a] Reference 7. [b] M. Rey, U. A. Huber, and A. S. Dreiding, *Tetrahedron Letters*, 3583 (1968). [c] H. Hart, J. D. DeVrieze, R. M. Lange, and A. Sheller, *Chem. Commun.*, 1650 (1968).

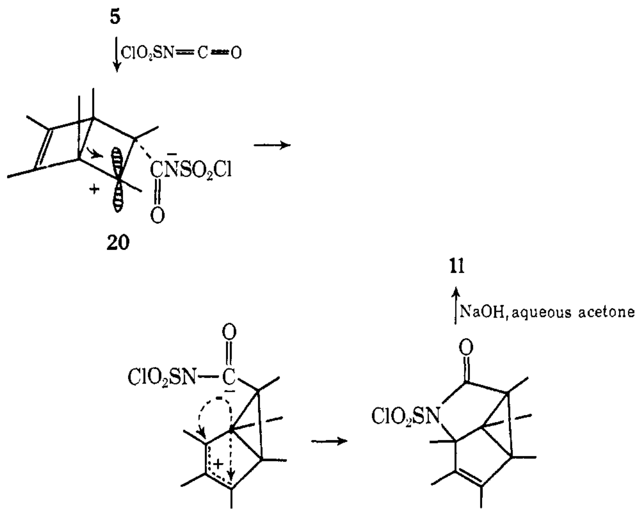
Chart I



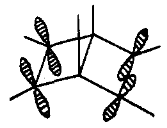
The most plausible mechanistic pathway available for the conversion of **5** to **11** requires initial electrophilic attack on **5** from its *endo* surface to give ion **20**. Subsequent or concomitant migration of the central bond in **20** now occurs, but to bypass a fundamental energetic objection,[12] this bond must become attached

(12) That is to say, the strained nature of the alternative transition state which would involve bonding to the lower lobe and result in formation of a *trans*-fused bicyclo[3.1.0]hexenyl cation is expected to

to the upper lobe of the vacant p orbital at C-2. This geometric restriction provides access to *cis*-fused bicyclo[3.1.0]hexenyl ion **21** in which the chlorosulfonylisocyanate residue occupies the *endo* configuration. C–N bond formation in **21** (two equivalent five-centered transition states are possible) with cancellation of charge is rendered particularly facile because of the existing favorable stereochemical arrangement. This combination of factors serves as an effective means of trapping reactive cations such as **6** and **21** at the appropriate point along the potential energy sufrace and provides conclusive evidence for their intervention.



The observed preferential *endo* attack of chlorosulfonyl isocyanate on hexamethyl (Dewar benzene) (**5**) is deserving of further comment. Electronic theory supplies an attractive explanation. Thus, the rigidly folded nature of **5** causes the p orbitals of the two π bonds to be held in close proximity on the lower surface of the molecule (*cf.* **23**) with the result that a greater concentration of electron density exists on the *endo* face. Electrophilic attack from that side of the molecule offering the greater electron density is expected to be favored.[13] The steric influence of the two methyl groups at the ring juncture positions may also act to favor *endo* approach. On this basis, the observation by Atkins and Burgess[9d] that ethyl N-sulfonylcarbamate bonds to **5** from its *exo* surface would seem difficult to explain.[14] Torsional effects[15] provide at least a partial solution to this dilemma. In the transition state for electrophilic attack from the *endo* side, the dihedral angle between the methyl groups at C-1 and C-2 is decreased, and torsional strain is generated (**24**). If *exo* attack occurs, a different torsional strain caused by steric compression of the electrophile and the C-1 methyl substituent arises (**25**). As a result, the actual *exo*/*endo* rate ratios in addition to **5** may be the result of carefully balanced electronic, steric, and torsional effects. In the absence of secondary confirmatory evidence, arbitrary designation of stereochemistry to products of addition to **5** and its congeners should therefore be avoided.



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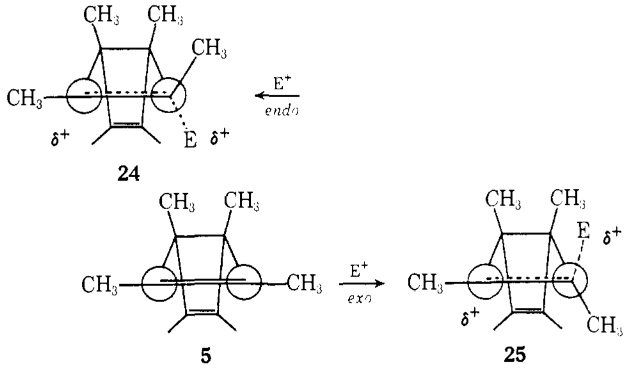
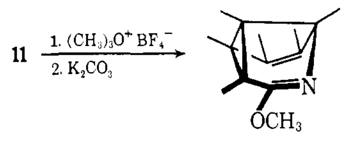


The azasemibullvalene **26** was prepared by treating **11** with trimethyloxonium fluoroborate in dry methylene chloride at room temperature. The nmr spectrum of **26** shows four sharp singlets at δ 3.66 (3 H), 1.32 (3 H), 1.22 (6 H), and 0.96 (3 H) and two singlets with additional small long range coupling at δ 1.67 (3 H) and 1.56 (3 H). The ultraviolet spectrum [$\lambda_{\max}^{C_2H_5OH}$ shoulder at 220 nm (ϵ 4000)] is closely similar to those observed for methoxyazabullvalene[4] and 1-azatricyclo[3.3.0.0^{2,8}]octa-3,6-diene.[16] The ultraviolet spectra of dihydrobullvalene[17] and semibullvalene[18] also provide satisfying parallel comparisons. The nmr spectrum of **26** remained unaltered from -40 to $+150°$. Thus, the restrictions imposed by the imino ether grouping in **27** on the possible Cope rearrangement parallel those observed with methoxyazabullvalene.[4]



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Rearrangement of Lactam 11. When stirred with boron trifluoride etherate in methylene chloride solution for 24–48 hr at ambient temperature, lactam **11** was smoothly rearranged to a mixture of three new lactams (tlc analysis). For ease of purification, this mixture was treated directly with trimethyloxonium fluoroborate and the derived imino ethers were separated by preparative scale gas chromatography: **29** (20%), **27** (75%), and **28** (5%).[19] Assignment of structure to the imino ethers depends almost solely on spectral data and careful hydrolytic reconversion of **27** and **29** back to their respective amides. From an intense

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preclude its operation in such a competitive situation. Mechanistic alternatives of this sort have been recognized previously in two somewhat related situations: K. B. Wiberg and A. J. Ashe, *Tetrahedron Letters*, 1553 (1965); R. N. McDonald and E. C. Reinecke, *J. Org. Chem.*, **32**, 1878 (1967).

(13) A similar theory has been advanced to explain preferential inside-tub approach by electrophilic reagents toward cyclooctatetraenes.[11a]

(14) The addition of 4-phenyl-1,2,4-triazoline-3,5-dione to **5** may actually follow a similar path.[9a]

(15) P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 699, 701 (1967).

(16) D. S. Wulfman and J. J. Ward, *Chem. Commun.*, 276 (1967).

(17) G. Schröder, *Chem. Ber.*, **97**, 3140 (1964).

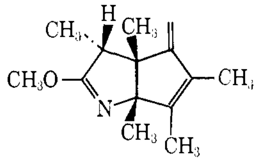
(18) H. E. Zimmerman and G. L. Grunewald, *J. Am. Chem. Soc.*, **88**, 183 (1966).

(19) This ratio of products was dependent on the duration of exposure of **11** to the boron trifluoride etherate. Although the quantity of **28** was always about 5%, the proportions of **27** and **29** were seen to vary (allylic rearrangement).

Table II. Nmr Chemical Shift Data for the Rearrangement Products of **11** ($CHCl_3$, δ Values)

Compd	Saturated methyl groups	Allylic methyl groups	$>CHCH_3$	$—OCH_3$	Vinyl protons
29	0.95 (d, J = 8 Hz) 1.22 (s) 1.24 (s)	1.69 (s) 1.83 (s)	2.47 (q, J = 8 Hz)	3.83	4.66, 5.00
27	0.97 (s) 1.02 (d, J = 8 Hz) 1.16 (s)	1.62 (s) 1.73 (s)	2.60 (q, J = 8 Hz)	3.63	4.44, 4.57
28	0.95 (s) 1.08 (d, J = 8 Hz) 1.27 (s)	1.60 (s) 1.60 (s)	2.48 (q, J = 8 Hz)	3.60	4.68, 4.78
35	0.98 (d, J = 8 Hz) 1.20 (s) 1.24 (s)	1.64 (s) 1.71 (s)	2.21 (q, J = 8 Hz)		4.60, 4.91
33	1.03 (s) 1.07 (d, J = 8 Hz) 1.13 (s)	1.65 (s) 1.72 (s)	2.32 (q, J = 8 Hz)		4.62, 4.72

ultraviolet absorption band at 239–240 nm exhibited by **27**, **28**, and **29** can be inferred the presence of a substituted conjugated diene moiety in each substance. Any question that the unsaturation be of a type involving the $-C(OCH_3){=}N-$ linkage was removed by comparing the spectrum of **33** which shows a maximum at 237 nm. Consideration of the mechanistically plausible paths of rearrangements that are open to **11**, coupled with the ultraviolet data, suggested that three imino ethers from the group **27–30** had been produced.



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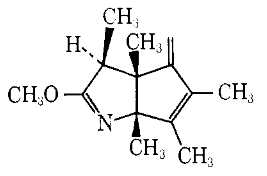

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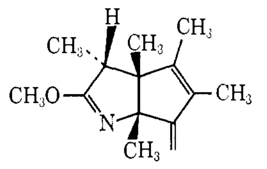

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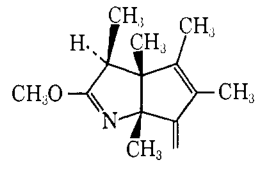

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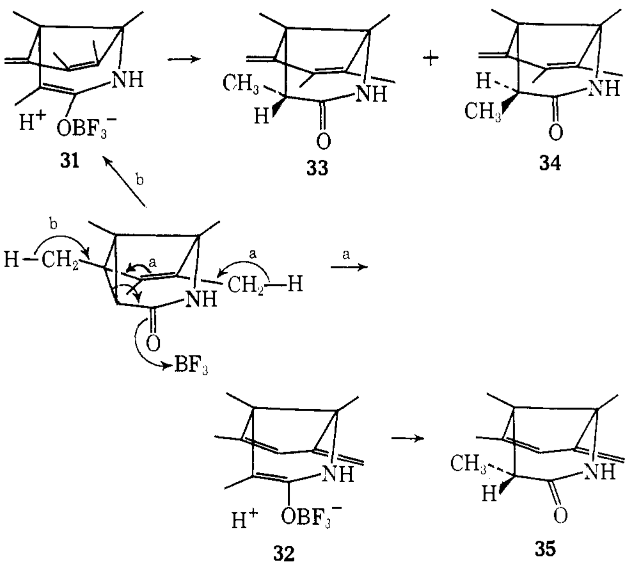
In the nmr spectra of each of the imino ethers (Table I), the presence of two vinyl protons, a combination of allylic and two saturated methyl groups, and a $>CHCH_3$ function was clearly evident. Strikingly, however, whereas the $\Delta\delta$ of the vinyl protons of **29** is 0.34, the values for **27** and **28** are 0.13 and 0.10, respectively. Lactams **35** and **33** give parallel $\Delta\delta$ values of 0.31 and 0.10, respectively.[20] The isomeric nature of imino ethers **27** and **28** is attested to by the close similarity of their spectra. The large vinyl proton chemical shift difference exhibited by **29** and **35** would seem to require that one vinyl proton reside in the vicinity of the nitrogen atom.

From consideration of Dreiding models, a theoretically calculable energy difference between the pairs **27**:**28** and **29**:**30** would appear to lie somewhere in the vicinity of 2.5 kcal/mole in favor of **27** and **29**.[21] Since the rearrangement of **11** must necessarily proceed by way of enol forms **31** and **32**, the opportunity for *exo* protonation is available to both intermediates.

The above considerations lead us to conclude tentatively that lactams **33** and **35** predominate and that **33** is produced in highest yield. The structures of the imino ethers follow directly from these assignments.



Experimental Section[22]

Addition of CSI to 5. To a cold (−15°) solution of 25.0 g (0.154 mole) of hexamethyl (Dewar benzene) (**5**) in 150 ml of dry methylene chloride was added dropwise with stirring under nitrogen a solution of 22.0 g (0.155 mole) of chlorosulfonyl isocyanate in 50 ml of the same solvent. The addition required 30 min. After an additional 15 min, the solvent was removed *in vacuo* at 0° or below. The crystalline residue was dissolved in 300 ml of acetone–water (3:1) and hydrolytic removal of the chlorosulfonyl group was achieved by titration with 4 *N* sodium hydroxide (pH meter). The mixture was extracted four times with chloroform (250 ml) and the combined organic layers were washed well with water, dried, and evaporated. Recrystallization of the resulting pale yellow solid (27.5 g 87%) from acetonitrile gave **11** as long white blades: mp 168–170°;

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[20] There was insufficient material available to study the hydrolysis of **28**. However, by careful subtraction of the vinyl proton absorption of **33** and **35** from the nmr spectrum of the crude lactam mixture, it was concluded that the lactam derivable from **28** possesses a $\Delta\delta$ of 0.12.

[21] This potential energy difference was calculated by subtraction of the *gauche* 1,3-methyl-methylene (or methyl) interaction in **27** and **29** (*ca.* 3.5 kcal/mole) from the nearly perfectly eclipsed vicinal methyl-methyl interactions in **28** and **30** (*ca.* 6 kcal/mole) [*cf.* N. L. Allinger and M. A. Miller, *J. Am. Chem. Soc.*, **83**, 2145 (1961)].

[22] The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer purchased with funds made available through the National Science Foundation. The preparative scale gas chromatographic separations were performed with a Varian Aerograph A-90P3 unit equipped with thermal conductivity detectors.

ν_{max}^{Nujol} 1690 cm^{-1}; uv end absorption; $\delta_{TMS}^{CDCl_3}$ singlets at 1.62 (6 H), 1.18 (3 H), and 1.05 (3 H).

Anal. Calcd for $C_{13}H_{19}NO$: C, 76.05; H, 9.33; N, 6.82. Found: C, 75.80; H, 9.43; N, 6.93.

Hydrogenation of 11. A 1.65 g (0.008 mole) sample of **11** in 100 ml of methanol was hydrogenated over 10% rhodium on carbon at 50 psig and 25°. After 36 hr, the catalyst was separated by filtration and the residue was recrystallized from ether–hexane to give white prisms of **13**: mp 155–155.5°; $\nu_{max}^{CHCl_3}$ 1690 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ *ca.* 2.1 (complex multiplet, 2 H), singlets at 1.16 (3 H) and 1.07 (9 H), and doublets (J = 7 Hz) at 0.90 (3 H) and 0.78 (3 H).

Anal. Calcd for $C_{13}H_{21}NO$: C, 75.31; H, 10.21; N, 6.76. Found: C, 75.44; H, 10.28; N, 6.73.

Epoxidation of 11. To a solution of 1.03 g (0.005 mole) of **11** in 10 ml of chloroform was added with stirring 1.2 g (0.0055 mole) of *m*-chloroperbenzoic acid. After stirring at room temperature for 2 hr, the solution was washed with 2 *N* sodium hydroxide solution and water, and dried. The filtrate was evaporated to give 720 mg (65.5%) of waxy white solid, mp 175–176°. Two recrystallizations of **14** from ether gave white prisms: mp 178–179°; ν_{max}^{Nujol} 1700 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ singlets at 1.29 (6 H), 1.21 (3 H), 1.15 (3 H), 1.04 (3 H), and 0.98 (3 H).

Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.55; H, 8.65; N, 6.33. Found: C, 70.45; H, 8.57; N, 6.27.

Permanganate Oxidation of 11. To a stirred solution of 2.05 g (0.01 mole) of **11** in 60 ml of reagent grade acetone was added 5 g of anhydrous magnesium sulfate. After cooling to 0°, a solution of 2.37 g (0.015 mole) of potassium permanganate in 40 ml of water was added dropwise. The mixture was stirred for an additional 30 min and filtered. The filtrate was concentrated under reduced pressure to remove most of the acetone and the remaining purple aqueous phase was extracted with chloroform. The combined organic layers were washed with water, dried, and evaporated. There was isolated 1.50 g (63.3%) of white solid, mp 128–135°. Two recrystallizations of this material from ether gave white prisms of **15**: mp 135–136.5°; $\nu_{max}^{CHCl_3}$ 1690 and 1715 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ singlets at 2.28 (3 H), 2.07 (3 H), 1.35 (6 H), and 1.22 (6 H).

Anal. Calcd for $C_{13}H_{19}NO_3$: C, 65.80; H, 8.07; N, 5.90. Found: C, 65.94; H, 8.33; N, 5.84.

Hofmann Degradation of 11. A solution of 3.1 g (0.015 mole) of **11** in 50 ml of dry dimethylformamide was treated with 720 mg (0.018 mole) of 60% sodium hydride–mineral oil dispersion (previously washed with ether) and the mixture was stirred at 70–80° for 2 hr. The heating was removed (cooling is not recommended at this point because crystallization of the salt occurs) and 4.3 g (0.030 mole) of methyl iodide was added slowly by means of a pipet below the surface of the solution. After stirring for 15 min, another 4.3 g of methyl iodide was added and the mixture was stirred at room temperature for 1 hr. Ether (200 ml) was added and the precipitated salts were filtered. The filtrate was evaporated under reduced pressure and the residue was distilled to give 2.80 g (85.4%) of **16** as a colorless liquid, bp 134° (0.15 mm). A center cut was submitted to analysis: $\nu_{max}^{CCl_4}$ 1670–1690 cm^{-1}; $\delta_{max}^{CDCl_3}$ singlets at 2.62 (3 H), 1.58 (6 H), 1.26 (6 H), 1.14 (3 H), and 1.01 (3 H).

Anal. Calcd for $C_{14}H_{21}NO$: C, 76.66; H, 9.65; N, 6.39. Found: C, 76.46; H, 9.78; N, 6.34.

A mixture of 380 mg (0.01 mole) of lithium aluminum hydride and 2.0 g (0.0091 mole) of **16** in 20 ml of anhydrous tetrahydrofuran was refluxed for 4 hr. With cooling, the complex was decomposed by the stepwise addition of 0.4 ml of water, 0.4 ml of 30% sodium hydroxide solution, and 1.2 ml of water. The solution was filtered and evaporated. The residue as dissolved in 30 ml of ether and 4 ml of methyl iodide was added. The methiodide salt began to precipitate immediately from solution. The mixture was refluxed for 30 min, cooled, and filtered. The white solid was recrystallized from ethanol–ether to give 1.6 g (50.4%) of **18** as white needles, mp 160–160.5°.

Anal. Calcd for $C_{15}H_{26}IN$: C, 51.87; H, 7.55; N, 4.03. Found: C, 51.99; H, 7.79; N, 3.89.

A 1.35-g sample of **18** was dissolved in water and the solution was passed through a column of Amberlite IRA-400 (hydroxide form). The alkaline aqueous eluate was concentrated under reduced pressure and the solid hydroxide was heated at *ca.* 135° (0.15 mm) to give a colorless liquid distillate which was converted directly to its perchlorate salt. Recrystallization of this material from ethanol–ether or water gave **19**·$HClO_4$ as shiny white platelets: mp 148°; $\delta_{TMS}^{acetone\text{-}d_6}$ collapsed AB doublet at 5.01 and 4.92 (2 H), and singlets at 2.90 (6 H), 1.78 (3 H), 1.68 (3 H), and 1.27 (9 H).

Anal. Calcd for $C_{15}H_{28}ClNO_4$: C, 56.33; H, 8.19; N, 4.38. C, 56.67; H, 8.27; N, 4.33.

Hexamethylmethoxyazasemibullvalene (26). A solution of 2.05 g (0.01 mole) of **11** in 20 ml of dry methylene chloride was treated with 1.92 g (0.013 mole) of trimethyloxonium fluoroborate and the resulting mixture was stirred in the absence of moisture for 6 hr. The solution was treated with excess 50% potassium carbonate solution and the organic layer was dried, filtered, and evaporated. Distillation of the residue afforded 1.68 g of colorless liquid, bp 68–70° (0.3 mm), which was converted in part to its perchlorate salt, mp 192–193° dec (from ethanol–ether).

Anal. Calcd for $C_{14}H_{22}ClNO_5$: C, 52.58; H, 6.94; N, 4.38. Found: C, 52.63; H, 6.99; N, 4.49.

Rearrangement of 11. A solution of 1.0 g (0.0049 mole) of **11** in 15 ml of methylene chloride containing 0.7 ml of boron trifluoride etherate was stirred at room temperature for 24 hr. The solution was washed with saturated sodium bicarbonate solution and water, dried, and evaporated. The mixture of lactams was converted directly to their imino ethers with trimethyloxonium fluoroborate as above. The imino ethers were separated by preparative gas chromatography on a 10 ft × 0.25 in. aluminum column packed with 20% SF-96 on 60/80 mesh Chromosorb G at 165–170°.

The first material to be eluted (20%) has been assigned structure **29**, $\lambda_{max}^{C_2H_5OH}$ 239 nm (ϵ 12,000). The picrate of **92** was obtained as pale yellow prisms from ethanol, mp 152–153°.

Anal. Calcd for $C_{20}H_{24}N_4O_8$:C, 53.57; H, 5.39; N, 12.50 Fouud: C, 53.60; H, 5.00; N. 12.15.

The second imino ether to be eluted (75%) has been assigned structure **27**, $\lambda_{max}^{C_2H_5OH}$ 240 nm (ϵ 14,000). The picrate of **27** was obtained as yellow crystals from ethanol, mp 158–159°.

Anal. Calcd for $C_{20}H_{24}N_4O_8$: C, 53.57; H, 5.39; N, 12.50. Found: C, 53.68; H, 5.31; N, 12.19.

A solution of 118 mg of **27** was refluxed with 2 ml of 2 *N* hydrochloric acid for 2 hr. The acid solution was extracted with chloroform and the combined organic layers were washed with saturated sodium bicarbonate solution and water, dried, and evaporated. The oil thus obtained crystallized on standing; recrystallization from ether–hexane gave white crystals of **33**: mp 168–169°; $\lambda_{max}^{C_2H_5OH}$ 237 nm (ϵ 13,200).

Anal. Calcd for $C_{13}H_{19}NO$: C, 76.05; H, 9.33; N, 6.82. Found: C, 75.82; H, 9.29; N, 6.68.

The third imino ether to be eluted (5%) has been assigned structure **28**, $\lambda_{max}^{C_2H_5OH}$ 240 nm (ϵ 16,000). The picrate of **28** was obtained as yellow crystals from ethanol, mp 152–153°.

Anal. Calcd for $C_{20}H_{24}N_4O_8$: C, 53.57; H, 5.39; N, 12.50 Found: C, 53.33; H, 5.56; N, 12.36.