Homotropilidenes. 3.[1] Synthetic and Structural Studies of Dihydroazabullvalenes

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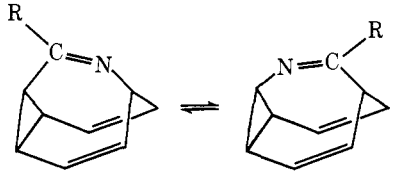
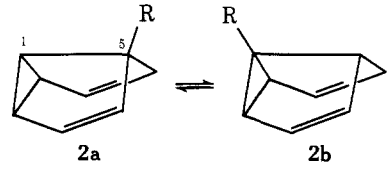
Abstract: Variously substituted dihydroazabullvalenes have been synthesized in order to determine the favored position of the Cope equilibrium of aza-bridged homotropilidines. The general synthetic route leading cleanly to dihydroazabullvalene derivatives (**4**) involves submission of 7-azabicyclo[4.2.2]deca-2,4,9-trien-8-ones (**3**) or 8-thiones (**8**) to ultraviolet irradiation using Pyrex optics and acetone sensitization. With a methylene group in the 8 position as in **10c**, acetone-sensitized photorearrangement through Pyrex is unsuccessful. Carbamate **10c** undergoes direct photorearrangement in methanol or acetone with Vycor or quartz optics to afford photoproducts **13–15** and in trace amounts the dihydroazabullvalene (**5c**). *N*-Benzyllactam (**4b**) can be converted to *N*-benzyldihydroazabullvalene (**5b**), its conjugate acid (**6**), and its *N*-oxide (**7**). An attempt to cleave the benzyl group from either **5b** or **10b** with methyl chloroformate led to **20**. Other attempts to cleave the benzyl group of **5b** were also unsuccessful. The favored tautomer of azabullvalenes has a nitrogen atom as its amide, free base, salt, or *N*-oxide bonded to the bridgehead carbon atom and adjacent carbonyl, thiocarbonyl, or methylene next to cyclopropyl.

Substituted azabullvalenes (**1**) have been found to undergo a ready Cope rearrangement between **1a** and **1b**, as well as more complex fluctional behavior at elevated temperatures.[3] In the case of R = ethoxy, structure **1a** is favored during low-temperature rearrangement by about 2 kcal/mol.[3b] Theoretical analysis[4] of substituent effects at positions 1 and 5 of the structurally related tautomeric semibullvalenes **2a** and **2b** has led to the prediction that electron donors R will shift the Cope equilibrium markedly toward **2a**, while electron acceptors will shift the equilibrium toward **2b**. In the polarized C=N double



1a **1b**



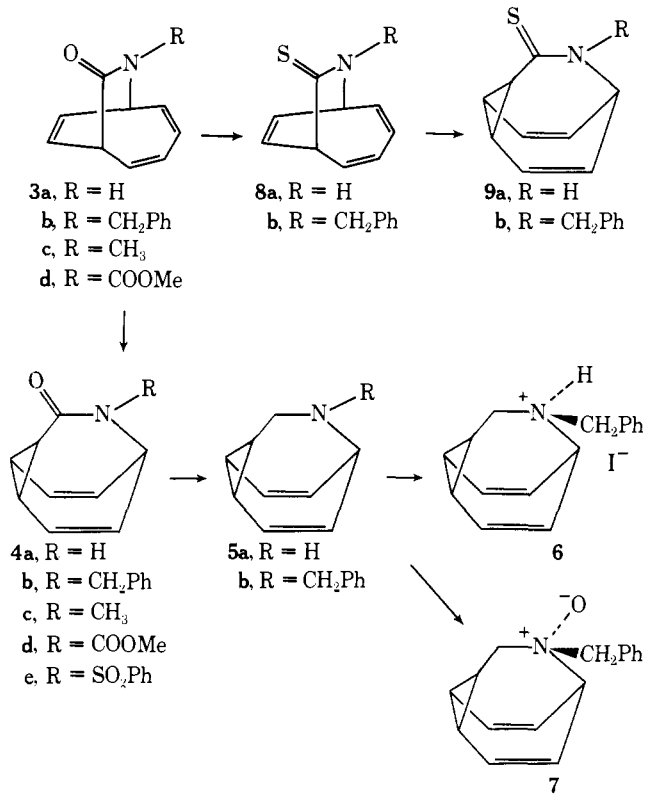
2a **2b**

bond of **1**, where it is clear that the carbon end is the electron acceptor and the nitrogen end the electron donor, an extended Hückel calculation favors **1a** over **1b** by 0.37 eV in agreement with the structural evidence. As part of an effort to survey substituent effects on Cope equilibria, we have synthesized a number of dihydroazabullvalenes related to **1** and determined their tautomeric preferences.

Synthetic Aspects

The desired dihydroazabullvalene derivatives (Table I) were synthesized from the readily available bicyclic lactam **3a**[3a] as outlined in Scheme I. Treatment of **3a** with sodium hydride in dimethylformamide, followed by addition of benzyl chloride (**3b**), methyl sulfate (**3c**), or methyl chloroformate (**3d**) and photorearrangement in acetone with a 450-W Hanovia high-pressure lamp with quartz or Vycor optics afforded dihydroazabullvane lactams **4b–d**. Aluminum hydride reduction of lactam **4b** gave *N*-benzyldihydroazabullvalene (**5b**),[5] which was protonated with trifluoroacetic acid to yield salt **6** or oxidized with *m*-chloroperbenzoic acid to *N*-benzylamine *N*-oxide (**7**). Lactam **3b** was converted to thiolactam **8b** with phosphorus pentasulfide in dioxane, and **8b** was photorearranged in acetone as above to give dihydroazabullvalene thiolactam (**9b**).

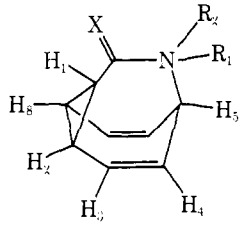
Scheme I. Synthesis of Dihydroazabullvalenes



As shown in Scheme II, thiolactam **8a**[3a] could be reduced with lithium aluminum hydride to amine **10a**. Reaction of amine **10a** with methyl chloroformate afforded carbamate **10c**, found to be contaminated with small amounts of carbamates **11** and **12** traced to overreduction during the synthesis of **10a**. *N*-Methylsulfonamide (**10d**) was prepared from the anion of **10a**[3a] using methanesulfonyl chloride.

Dihydroazabullvalene carbamate (**5c**) was prepared by photoirradiation of carbamate **10c** through Vycor or quartz optics with a 450-W Hanovia lamp for 8 h in acetone or methanol. The photoproducts from **10c** are shown in Scheme III with relative yields indicated in parentheses. The NMR

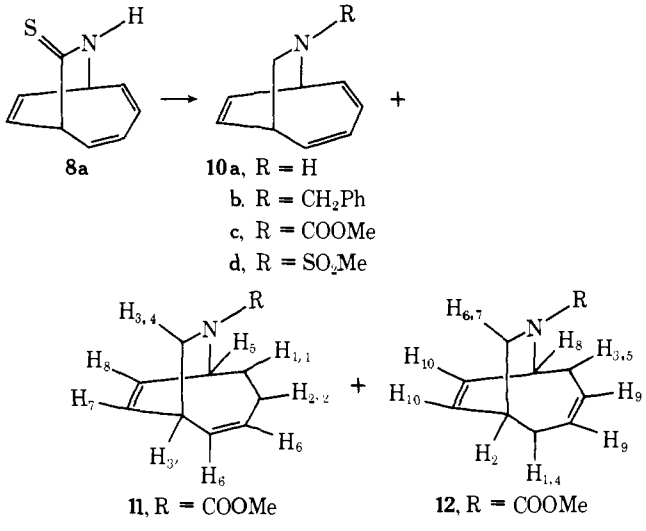
Table I. 100-MHz Proton NMR Spectra of Dihydroazabullvalenes ($CDCl_3$)



Compd	X	R_1	R_2	δ H_1	δ $H_{2,8}$	δ H_5	DNMR behavior
4b	O	CH_2Ph		3.04[a]	2.44	3.54[b]	c
4c	O	CH_3		2.88	2.32	3.44[d]	e
4d	O	CO_2CH_3		2.95	2.38	4.95[f]	g
4e	O	SO_2Ph		2.87[h]	2.42	5.04[i]	g
5b	HH	CH_2Ph		1.94[j]	2.52	3.14[k]	l
5c	HH	CO_2CH_3		2.06[m]	2.83	4.33[n]	g
6	HH	CH_2Ph	H	2.27[o]	2.27	3.95[n]	p
7	HH	CH_2Ph	O	1.07	1.46	4.63	q
9	S	CH_2Ph		3.94[a]	2.45	3.75[b]	q

[a] t, J = 9 Hz. [b] t, J = 8 Hz. [c] No signal averaging to 70°, then some decomposition. [d] Simplifies upon irradiation of H_3/H_4. [e] No signal averaging from −70 to 140° ($CDCl_3$). [f] Irradiation of H_4 (δ 6.03) collapses H_5 to a singlet. [g] No signal averaging in α-chloronaphthalene to 120°. [h] $J_{1,2}$ = 9 Hz. [i] $J_{4,5}$ = 5 Hz. [j] m, $J_{1,X}$ = 4.0 Hz, $J_{1,2}$ = 9 Hz. [k] t, $J_{4,5}$ = 8 Hz discernible upon addition of 20 mol % trifluoroacetic acid. [l] No signal averaging in α-chloronaphthalene 30–160 °C. [m] $J_{1,2}$ = 4 Hz; [n] $J_{4,5}$ = 8 Hz. [o] Multiplet. [p] Amine 5b (75 mg) in $CDCl_3$ (0.5 ml) with trifluoroacetic acid (160 mg), no averaging to 70°, then decomposition; [q] No shift averaging to 70°.

Scheme II. Products from Reduction of Lactam 8a



8a → **10a**, R = H; **b**, R = CH_2Ph; **c**, R = COOMe; **d**, R = SO_2Me + **11**, R = COOMe + **12**, R = COOMe

spectra of the photoproducts are partially described in Table II. With a Pyrex filter less than 2% reaction to the same mixture occurred after 24 h. Sulfonamide **10d** behaved similarly to **10c**; irradiation in acetone with Pyrex optics afforded only starting sulfonamide while irradiation in methanol or acetone with quartz or Vycor optics afforded a complete mixture.

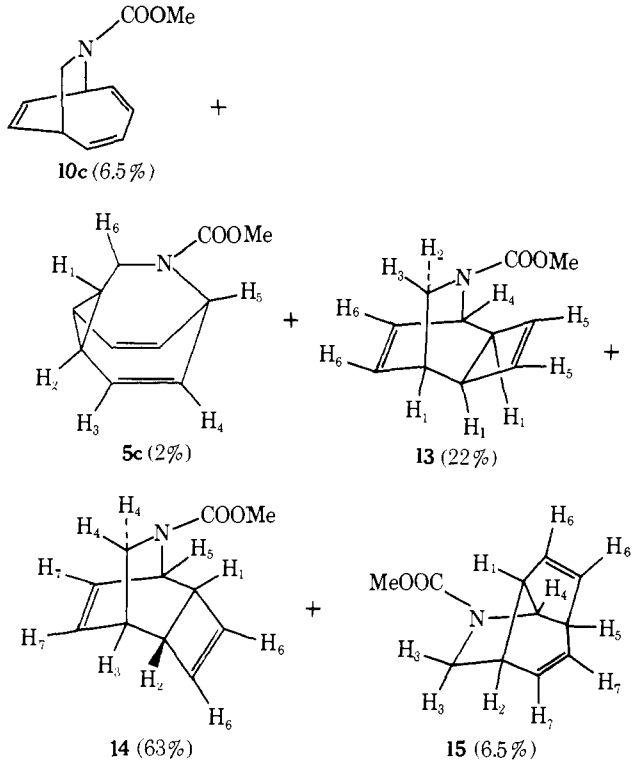
Attempted Cleavage of the Benzyl Group of 5b. Attempts to cleave the benzyl group of **5b** to afford **5a** were unsuccessful. Cyanogen bromide[6] and phenyl chloroformate[7] afforded complex mixtures. Hydrogenolysis[8] in acetic acid with or without added perchloric acid at 1 atm resulted in olefin reduction. Oxidative debenzylation with manganese dioxide,[9] *N*-bromosuccinimide,[10] dimethyl azodicarboxylate,[11] lead tetraacetate,[12] triphenylcarbonium tetrafluoroborate,[13] or potassium ferricyanide[14] failed. A novel rearrangement with **5b** and mercuric acetate has been reported.[5] Reaction of either

Table II. 100-MHz Spectra of 10c Photoirradiation Products

Absorption	Shift description, δ 5c[a]	13[b]	14[a]	15[a]
H_1	2.06 (m)	2.77 (s)	3.10 (m)	1.52 (d,t)[c]
H_2	2.83 (m)	3.11 (d)[d]	2.72 (m)	2.00 (q)[e]
H_3	5.83 (m)	3.86 (d)[f]	3.10 (m)	3.29 (m)[g]
H_4	5.15 (t)[h]	5.13 (m)	3.64 (m)[f]	3.29 (m)[g]
H_5	4.33 (t)[i]	6.54 (d)[j]	4.70 (m)	3.97 (s)
H_6	3.93 (d)[k]	6.66 (d)[j]	5.84 (s)	5.82 (m)
H_7			6.04 (t)[k,l]	6.13 (m)[m]

[a] $DCCl_3$, 76°. [b] Benzene-d_6, 76°. [c] J = 6, 2 Hz. [d] J = 11 Hz. [e] J = 7, 4 Hz. [f] Partially buried under OMe. [g] Irradiation collapses H_2 to a d, J = 7 Hz. Sharpens H_7 and H_1. [h] J = 10 Hz. [i] J = 8 Hz. [j] J = 2 Hz. [k] J = 4 Hz. [l] Collapses to a d, J 4 Hz upon irradiation of H_7. [m] Irradiation simplifies H_1 to a t, J = 6 Hz.

Scheme III. Photoproducts of 10c (Methanol)



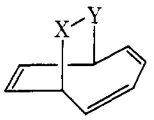
10c (6.5%) + **5c** (2%) + **13** (22%) + **14** (63%) + **15** (6.5%)

5b or **10b** with methyl chloroformate afforded **20** upon high-temperature workup. A plausible mechanism for formation of **20** is shown in Scheme IV. Acylation of either **5b** or **10b** on nitrogen followed by carbon–nitrogen bond cleavage will lead to the same homotropilium cation species **16**. This species can be trapped by chloride ion to form a mixture of halogenated products **17**. Loss of hydrogen chloride from the intermediates **17** can be expected to afford molecules such as **19**, which can thermally rearrange to **20**. Alternately, loss of chloride to generate cations **16** or **18**, followed by loss of a proton and rearrangement[15] can lead to **20**. The structure of **20** was confirmed by alkylation of methyl *N*-benzylcarbamate with 1-chloro-3-phenyl-2-propene.

Discussion

Photochemical Results. Carbamate **10c** is the only substrate in Table III which fails to undergo cleanly acetone triplet-sensitized di-π-methane photorearrangement to a bullvalene or dihydroazabullvalene structure. The ultraviolet spectrum of **10c** is typical of other compounds in Table III. However, Dreiding molecular models indicate the saturated methylene bridge (X = CH_2) renders **10c** more flexible than the other

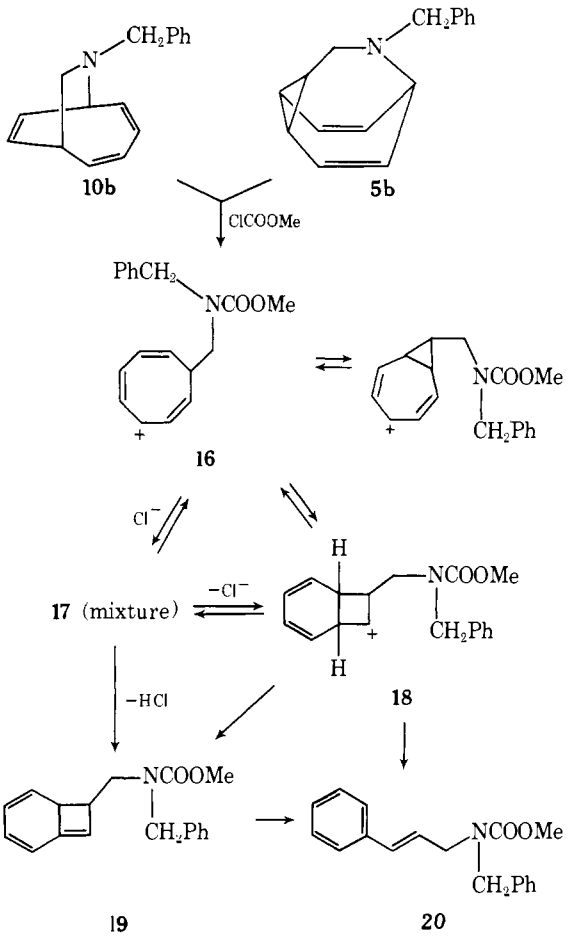
Table III. Ultraviolet Spectra of Bicyclo[4.2.2]deca-2,4,7-trienes



Compd	X–Y	Uv spectrum λ_{max}, nm	ϵ	Ref
3a	CO–NH	266[a]	3100	*c*
3b	CO–NCH_2Ph	268,[b] 259	3900, 3900	*d*
3d	CO–NCO_2Me	254,[b] 264(sh)	3500, 1750	*e*
10c	CH_2–NCO_2Me	264[b]	3100	*e*
25	MeSCH=N	282[a]	1710	*f*
26	MeOCH=N	271[a]	2000	*f*
27	CH=CH	280,[b] 268, 258	2900, 4200, 4200	*g*

[a] Acetonitrile. [b] 95% ethanol. [c] L. A. Paquette and T. J. Barton, *J. Am. Chem. Soc.*, 89, 5480 (1967). [d] Reference 5, this paper. [e] This work. [f] Reference 3a, this paper. [g] Reference 17b, this paper.

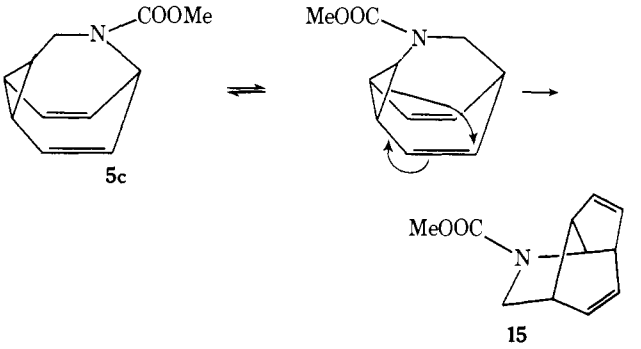
Scheme IV. Cleavage of Benzylamines 5b and 10b to 20



entries and triplet-sensitized di-π-methane rearrangements are known to be generally less efficient as the flexibility of the π system increases.[16] A carbonyl or double bond substituent located in the nonreacting bridge of the di-π-methane system and capable of conjugation with a cyclopropane diradical intermediate is a second factor lacking in **10c**, although present in the other 7-azabicyclo[4.2.2]deca-2,4,9-trienes of Table III. The ability of more rigid systems to undergo di-π-methane rearrangement without this extra conjugation suggests the latter is not significant.[17]

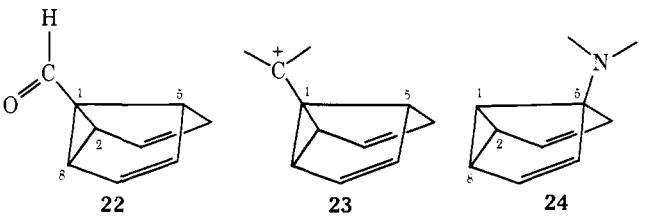
Direct unsensitized irradiation of **10c** affords a mixture of photoproducts **5c, 13, 14,** and **15**. The structures assigned to the photoproducts in Scheme III are those in agreement with

Scheme V. Mechanistic Route Leading to Dihydroazalumibullvalene (15)



NMR chemical shift and spin decoupling experiments summarized in Table II. These structures are analogous to those described previously obtained by photoirradiation of methoxyazabullvalene.[18] Dihydroazabullvalene (**5c**) is a minor product formed by di-π-methane rearrangement of **10c**. Cyclobutenes **13** and **14** are derived by disrotatory cyclization of **10c**. The simplest path to dihydroazalumibullvalene (**15**) involves a 1,3 shift mechanism shown in Scheme V from the less stable tautomer of **5c**.

Tautomeric Behavior. As noted in Table I all the dihydroazabullvalenes investigated exist with the nitrogen atom bonded at C(5) away from the cyclopropyl ring. This experimental result can be discussed in the context of the theoretical approach of Hoffmann and Stohrer,[4] which has predicted effects of C(1,5) bridgehead substituents on the equilibrium preferences of semibullvalene valence tautomers. In their analysis it was proposed that the Walsh orbitals of the cyclopropane portion of the semibullvalene interact in a π manner at C(1) with π-acceptors R to strengthen the 2,8 bond and favor the corresponding tautomer. A π donor R at C(1) weakens the 2,3 bond and disfavors the tautomer. A number of specific predictions made by Hoffmann and Stohrer[4] are relevant to the present discussion. Thus, for **22** when the carbonyl group is coplanar with C(1) and C(5), calculations favor the C(1) carbonyl substituted isomer by 0.43 eV relative to the C(5) isomer. The geometrically analogous cation **23** is favored over its tautomer by 0.72 eV. The theoretical prediction for 1(5)-aminosemibullvalene (**24**) indicates for the planar bisected amine geometry corresponding to the transition state for amine inversion (the nitrogen lone pair parallel to the 2,8 bond) the 5-aminosemibullvalene (**24**) is 0.12 eV more stable than the 1-aminosemibullvalene.[4]



It is of interest to extend the above theoretical predictions to dihydroazabullvalenes. Extrapolation of the results from models **22** and **24** to dihydroazabullvalene lactams **4b–e** and thiolactam **9** suggests attachment of carbonyl at C(1) and nitrogen at C(5) as found. Model **24** also predicts the observed preferential attachment of the lone endocyclic amino substituent at C(5) of amine **5b** and carbamate **5c**.

The lone-pair donor orbital of nitrogen and the low-lying π^* orbital of the carbonyl are easily singled out in classifying these substituents as donor or acceptor dominant,[19] but classification of the nitrogen atom in ammonium ion **6** and amine *N*-oxide **7** as donor or acceptor dominant presents a different problem. The nitrogen would not appear to be a good π donor.

Rather than a nitrogen lone-pair donor orbital there is now in **6** a hydrogen–nitrogen bond and in **7** a nitrogen–oxygen bond. The bonded electrons on nitrogen would appear to have less potential for electron donation. Moreover, even though π-electron attraction by the positively charged quaternary nitrogen atoms in **6** and **7** might be expected, the π-acceptor effect is likely to be small relative to that in model **23**. The tetracoordinate nitrogen atoms in **6** and **7** are not isoelectronic with a tricoordinate carbenium ion (**23**) having an empty orbital on carbon available as π acceptor.

Although the experimental results can be taken to imply that the formally positive nitrogen atom at C(1) has a destabilizing effect on the 2,8 bond, it is not clear this results from a π-donor interaction since other factors may play dominant roles.[20] The orientation of nitrogen at C(5) might be attributed to an adverse electron withdrawing effect associated with having the more electronegative cyclopropyl carbon ($sp^{2.27}$) C(1) adjacent to an electronegative nitrogen. The bridgehead carbon C(5) (sp^3) is better able to satisfy the electronic requirements of electronegative nitrogen atoms by an inductive mechanism.[3a]

Experimental Section

The NMR spectra were determined on a Varian XL-100-15 spectrometer using tetramethylsilane (Me_4Si) as internal standard. Solutions of 5–10% solute in $CDCl_3$ were used for NMR measurements unless otherwise specified. Couplings and coupling constants were, where necessary, obtained with the aid of decoupling experiments and temperature averaging of spectra. Uv spectra were recorded in 95% ethanol on a Cary 14 spectrometer. Melting points and boiling points are uncorrected.

General Procedure for Conversion of 3a to *N*-Substituted Bicyclo[4.2.2] Lactams 3b–d. Lactam **3a**[3a] (0.027 mol) and sodium hydride 57% oil dispersion (0.028 mol) in dry dimethylformamide (100 ml) were heated at 65° for 1 h and cooled to 45°, and alkyl or acyl halide (0.030 mol) was added. After 8 h at 45° the reaction mixture was filtered to remove sodium chloride, solvent was removed under vacuum, and the residue purified by crystallization, distillation, or VPC. Lactam **3b** was prepared as described previously.[5]

***N*-Methyl Lactam 3c.** Alkylation of lactam **3a** (13.0 g, 88 mmol) with methyl sulfate (11.1 g, 88 mmol) afforded an oil which was washed with pentane and distilled at 98–102 °C (0.25 mm) to give 3.95 g (28%) of an oil **3c**. White crystals, mp 75–76 °C, formed upon addition of ether to the oil; ir ($CHCl_3$) 1660 cm^{-1}; NMR δ 2.8 (NCH_3), 3.57 (1 H), 4.0 (t, 1 H), 5.2–6.5 (6 H).

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.48; H, 6.88; N, 8.72. Found: C, 74.77; H, 7.06; N, 8.64.

General Procedure for Preparation of *N*-Substituted Dihydroazabullvalenes 5a–d. A solution of lactam **3a–d** (1.5 g) dissolved in 300 ml of acetone was irradiated for 6–24 h with a 450-W high-pressure Hanovia lamp with quartz or Vycor optics. Removal of solvent afforded material which was purified by crystallization or VPC. Compounds **4a**,[3a] **4b**,[3a] and **5b**[5] were prepared as previously described.

***N*-Methyldihydroazabullvalene Lactam (4c).** Lactam **3c** (1.5 g) was irradiated for 6 h in acetone to afford a yellow oil on workup. Addition of ether afforded a white solid, **4c**, mp 100–101 °C: ir ($CHCl_3$) 1635 cm^{-1}; NMR δ 5.90 (4 H), 2.92 (3 H) (see Table I). Upon incremental addition of $Eu(dpm)_3$ to an NMR solution of **4c**, H_1 (closer to carbonyl) has an enhanced downfield shift relative to H_5 (close to nitrogen). At 0.61 M **4c** with 0.11 M $Eu(dpm)_3$, H_1 appears δ 1.2 downfield of H_5.

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.48; H, 6.88; N, 8.72. Found: C, 74.47; H, 6.92; N, 8.72.

***N*-Carbomethoxydihydroazabullvalene Lactam (4d).** Lactam **3a** (2 g, 15 mmol) was converted to its amide ion according to the general procedure and reacted with methyl chloroformate (1.9 g, 20 mmol). Workup afforded an oil which was purified by preparative TLC on silica gel (R_f 1.25, 60:40 tetrahydrofuran/cyclohexane) to afford a waxy solid **3d**, 1.2 g (43%): uv (95% ethanol) λ_{max} 254 (ϵ 3500), 264 nm (shoulder) (ϵ 1750); ir (CCl_4) 1675, 1740 cm^{-1}; NMR δ 4.18 (s, 3 H), 3.71 (dd, J = 6 and 9 Hz, 1 H), 4.29 (t, J = 6 Hz, 1 H), 5.40–6.40 (m, 6 H). Irradiation of **3d** (125 mg) in acetone (25 ml) for 24 h according to the general procedure with Pyrex optics (2 mm) yielded after filtration through alumina, removal of solvent, and crystallization from tetrahydrofuran/pentane, 80 mg (64%) of **4d**, mp 127–128 °C; ir (CCl_4) 1675, 1740 cm^{-1}; NMR δ 6.06 (m, 4 H), 3.76 (3 H) (see Table I).

An alternate synthesis of **4d** involved reaction of lactam **4a**[3a] (1 g, 7.2 mmol) with methyllithium (3 ml, 2.43 M in ether, 7.3 mmol) in dry tetrahydrofuran (50 ml), cooling to −76°, and slowly adding methyl chloroformate (0.75 g, 7.2 mmol). The solution was allowed to warm slowly to room temperature over 1 h. Workup afforded **4d**, 500 mg (48%).

Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.33; H, 5.44; N, 6.84.

***N*-Benzenesulfonyldihydroazabullvalene Lactam (4e).** Methyllithium (2 ml of 2.43 M in ether) was added to lactam **4a** (0.5 g, 3.6 mmol) in ether (30 ml). The solution was cooled to −76° and benzenesulfonyl chloride (0.70 g, 4 mmol) was added dropwise. The solution was allowed to warm to room temperature and then refluxed for 2 h. Removal of solvent, extraction of the residue with hot benzene, and evaporation of solvent afforded upon recrystallization from tetrahydrofuran/hexane 400 mg (68%) of **4e**, mp 178–179.5 °C: ir (Nujol) 1670, 1330, 1160 cm^{-1}, NMR δ 7.86 (2 H), 7.47 (3 H), 6.13 (m, 4 H), and Table I.

Anal. Calcd for $C_{16}H_{13}NO_3S$: C, 62.70; H, 4.56; N, 4.88. Found: C, 62.71; H, 4.61; N, 4.83.

***N*-Benzyldihydroazabullvalene *N*-Oxide (7).** *N*-Benzyldihydroazabullvalene (**5b**) (0.5 g, 2.2 mmol), prepared from *N*-benzyl lactam **4b** as previously described,[5] and *m*-chloroperbenzoic acid (0.4 g, 2.2 mmol) were allowed to react at 30° in methylene chloride. After 8 h ether was added and the solution was washed twice with 30 ml of 10% NaOH. Drying and removal of solvent yielded an oil which was digested with petroleum ether and filtered through alumina. Crystallization from petroleum ether gave solid **7**, mp 73–76 °C, 450 mg (84%): ir (CCl_4) 965 cm^{-1}; NMR δ 5.90 (s, 4 H), 3.74 (dd, J = 13 Hz, 2 H), 3.08 (dd, J = 8 Hz, 1 H) 2.62 (dd, J = 4 and 12 Hz, 1 H) (see Table I).

Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.28; H, 7.16; N, 5.92.

***N*-Benzyldihydroazabullvalene Thiolactam (9b).** *N*-Benzyl lactam **3b** (10 g, 0.04 mol) and P_2S_5 (10 g, 0.045 mol) were stirred in *p*-dioxane (300 ml) at room temperature for 48 h. The solid was filtered and washed with two 200-ml portions of benzene. Solvent was removed and the residue extracted with four 100-ml portions of hot benzene. Evaporation of solvent afforded 5.8 g (54%) of **8b**, mp 140–142 °C from benzene: NMR δ 4.22 (m, 1 H), 4.58 (m, 1 H), 4.62 (d, J = 15 Hz, 2 H), 5.66–6.5 (m, 6 H) 7.26 (s, 5 H).

Anal. Calcd for $C_{16}H_{15}NS$: C, 75.85; H, 5.97; N, 5.53. Found: C, 75.68; H, 5.92; N, 5.42. Thiolactam **8b** (2 g) in 500 ml of acetone was irradiated with a Pyrex filter for 2 h according to the general procedure to afford upon workup thiodihydroazabullvalene lactam **9b**, 1.1 g (55%), mp 113–114 °C from benzene: NMR δ 6.08 (m, 2 H), 5.70 (dd, J = 8 and 10 Hz, 2 H), 5.42 (s, 2 H), (see Table I). In an alternate synthesis of **9b**, *N*-benzyl lactam **4b**[5] (10 g, 0.042 mol) and P_2S_5 (10 g, 0.045 mol) were stirred in *p*-dioxane (300 ml) at room temperature for 48 h. Workup as above afforded solid **9b**, 6.5 g (61%).

Anal. Calcd for $C_{16}H_{15}NS$: C, 75.85; H, 5.97; N, 5.53. Found: C, 75.81; H, 5.92; N, 5.42.

Derivatives of 7-Azabicyclo[4.2.2]deca-2,4,9-triene (10a). Thiolactam **8a** (1 g, 6.8 mmol)[3a] and lithium aluminum hydride (0.5 g, 13 mmol) were stirred in diethyl ether (40 ml) at room temperature for 10 h. Workup afforded **10a**, 0.6 g (75%): NMR δ 3.75 (t, J = 6 Hz, 1 H) 3.22 (dd, J = 12 and 2 Hz, 1 H), 2.98 (dd, J = 12 and 4 Hz, 1 H), 2.70 (m, 1 H).

Utilizing standard procedures, amine **10a** and methyl chloroformate afforded carbamate **10c** as an oil: uv λ_{max} 266 nm (ϵ 3100); ir (CCl_4) 1710 cm^{-1}; NMR δ 2.92 (m, 1 H), 3.14 (dd, J = 12 and 4 Hz, 1 H), 3.72 (s, 3 H), 4.04 (t, J = 12 Hz, 1 H), 4.56 (m, 1 H), 5.68–5.98 (m, 6 H).

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.33. Found: C, 69.24; H, 6.55; N, 7.62.

By standard procedure, amine **10a** and methanesulfonyl chloride afforded methanesulfonamide **10d**, mp 72–74 °C (EtOH): NMR δ 2.94 (m, 1 H), 3.24 (dd, J = 4 Hz, 11 Hz, 1 H), 3.70 (dd, J = 11 and 1 Hz), 4.64 (t, J = 6 Hz, 1 H), 5.50–6.10 (m, 6 H).

Anal. Calcd for $C_{10}H_{13}NSO_2$: C, 56.85; H, 6.20; N, 6.63. Found: C, 56.73; H, 6.24; N, 6.45.

Irradiation of Carbamate 10c. Photoirradiation of **10c** (2g) in 500 ml of acetone or methanol for 8 h through a Vycor filter (according

to the general procedure) afforded 1.18 g (59%) of a mixture of photoproducts. Analysis of the product mixture (Scheme III) was made using GLC (4 m × ¼ in., 1.5% XF 1150 Chrom G, 180°). Identified were **5c** (14.4 min), **13** (6.4 min), **14** (7.0 min), **15** (13 min), and **10c** (10 min): ir (CCl_4) 1690 cm^{-1}; mass spectrum *m/e* 191; NMR results in Table II. Carbamates **13** and **14** were separated by multiple GLC separations at 120°. A trace was found of carbamate **11,** t_R = 7.3 min (3% of total yield): mass spectrum *m/e* 193; ir (CCl_4) 1690 cm^{-1}; NMR δ 1.83 (m, H_1), 2.29 (m, H_2), 3.00 (m, $H_3 + H_3'$), 3.65 (d, J = 12 Hz, H_4 and OCH_3), 4.57 (m, J = 6 Hz, H_5), 5.65 (m, H_6), 5.94 (m, J = 6 and 9 Hz, H_7), 6.20 (dd, J = 6 and 9 Hz, H_8). Irradiation of H_5 collapses H_8 to a d, J = 9 Hz, and sharpens H_1. Irradiation at H_3' collapses part of H_6 to a d, J = 12 Hz, and H_7 to a d, J = 9 Hz. Carbamate **12,** t_R = 9.2 min (1% of total yield); *m/e* 193; ir (CCl_4) 1680 cm^{-1}; NMR δ 2.16 (m, H_1), 2.45, 2.55 (br, H_2, H_3, H_4), 3.03–3.26 (m, H_5, H_6), 3.79 (d, H_7), 3.68 (OCH_3), 4.57 (br, H_8), 5.39 (s, H_9), 6.01 (m, H_{10}), was also obtained. These compounds were derived from overreduction of **8a** in the synthesis of **10a**. Only starting **10c** was recovered from photoirradiation (8–24 h) through Pyrex optics with the following combinations of solvent and/or sensitizer: acetone (2% trace of rearrangement mixture), methanol, hexane/acetophenone, or hexane/benzophenone.

Quantities of sensitizer were sufficient to absorb 99% of the light at 300 mm. Irradiation of **10c** through Pyrex in chloroform, bromoform, or 1-bromo-2-chloroethane gave no change. Replacement of the Pyrex filter by Vycor or quartz filter results in the mixture of products in Scheme III. The photoirradiation behavior of methanesulfonamide **10d** parallels that of **10c**. Photoirradiation of **10d** through Vycor for 8 h gave a product mixture which was not separated into its product mixture components. However, neither the downfield triplets characteristic of the olefinic region of dihydroazabullvalenes nor peaks corresponding to **10d** were observed in the NMR spectrum of the major components of the mixture isolated by silica gel TLC.

Attempted Synthesis of Dihydroazabullvalene 5a. *N*-Benzylamine **5b**[5] (1 g, 4.5 mmol) in methylene chloride (50 ml) was reacted at room temperature with methyl chloroformate (0.47 g, 5 mmol) for 8 h. Removal of solvent, addition of ether (75 ml), washing with 10% sodium bicarbonate (4 ml), drying, and removal of solvent afforded 1.3 g of a viscous oil; TLC (silica gel, 20:80 ether/pentane) indicated numerous components. Either by treatment with excess potassium *tert*-butoxide in dimethyl sulfoxide followed by VPC or by direct pyrolysis during VPC (2 m × ¼ in. 3% SF 96 Chrom W, 195° CT) there was isolated **20,** 350 mg (45 and 30%): ir (CCl_4) 1720 cm^{-1}; NMR δ 3.74 (s, 3 H), 3.97 (d, J = 6 Hz, 2 H), 4.49 (s, 2 H), 6.07 (d, J = 16 Hz, t, J = 6 Hz, 1 H), 6.40 (d, J = 16 Hz, 1 H), 7.24 (s, 5 H).

N-Benzylamine **10b** and methyl chloroformate in methylene chloride reacted as above to afford **20**. An independent synthesis of **20** involved conversion of methyl benzylaminecarbamate to its anion with sodium hydride in dimethylformamide and subsequent alkylation with cinnamyl chloride.

Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.85; H, 6.96; N, 5.21.

Acknowledgment. We thank George MacDonald, Johnson Foundation, University of Pennsylvania, for aid with the 220-MHz spectra, and R. Foltz of Battelle Memorial Institute Mass Spectroscopy Laboratory. This problem was originally conceived by L. A. Paquette.

References and Notes

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