Equilibrium Imbalances Arising from 2,8-Bridging by Aliphatic Chains of the Semibullvalene Nucleus[1]

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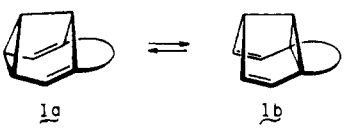
Abstract: To this time, bracketing effects have been applied only to systems which already experience large equilibrium displacements in the absence of the bridging chain. To probe the effect of various aliphatic bridges under conditions independent of this overriding force, four 2,8-annulated semibullvalenes have been synthesized from the structurally derived [4.2.*x*]propellatrienes by a reaction sequence involving in its key step the Ag^+-catalyzed isomerization of 9,10-diazabasketanes. Variable-temperature pmr studies of the four hydrocarbons gave indication of a unique dependence of their equilibria on temperature. For the cases where X = $(CH_2)_4$, and X = $CH_2CH{=}CHCH_2$, only limited spectral changes were noted. However, the preferred directions of equilibrium were diametrically opposite, the tetramethylene derivative favoring valence isomeric form **1a** and its unsaturated counterpart form **1b.** In these examples, entropy control operates throughout the entire temperature range examined. For the other two congeners, enthalpy and entropy factors are seen to oppose each other and to become essentially equal at a given temperature. As concerns the trimethylene bridged system, conditions above −29° (CS_2 solution) are such as to favor the $T\Delta S°$ term and valence tautomer **1b,** X = $(CH_2)_3$, dominates the equilibrium. Below this temperature, a preference for **1a** is noted as a consequence of enthalpy control. Interestingly, the pentamethylene derivative, X = $(CH_2)_5$, exhibits comparable features but in opposite directions. The causative factors are dissected into varying $\Delta H°$ and $\Delta S°$ components. In our estimation, these results comprise the first set of data showing that a diminution in "bracketing strain," as previously defined, need not necessarily correlate with an enhanced concentration gradient of the relevant tricyclic valence tautomer.

The extraordinary level of current chemical interest in semibullvalenes arises as a consequence of the unique structural and geometric features of the ring system which provide for Cope rearrangement to proceed with very low activation energy (6 kcal/mol[3] and below).[4,5] As demonstrated in an accompanying paper,[6] monosubstitution of the semibullvalene framework leads to pronounced ground state equilibrium displacements as a consequence of electronic influences operating on the various ring bonds. The subject matter of this paper deals with the application of our positionally selective synthetic process[1,6-8] to the preparation of 2,8-bridged semibullvalenes. Bracketing effects have had a history of providing useful data for the interpretative analysis of valence isomeric phenomena. Table I records selected examples of case studies. Vogel initially demonstrated that annulation of a cycloheptatriene ring at its 1 and 6 positions with a trimethylene chain imposes sufficient strain to restrict the molecule to its valence tautomeric norcaradiene form.[9] Lengthening of the chain to four methylene units results in strain release adequate to allow for complete reversal in favor of the bicyclic structure.[10] However, such equilibria are quite sensitive to the "pinching effect" exerted by the central bridge. For example, the related cyclooctatetraene–bicyclo[4.2.0]octatriene system with its unsaturated diatomic unit does not attain bicyclic characteristics until five sp^3-hydridized carbon atoms comprise the bracket.[11] In the nitrogen analog, the azapropellane form is favored until $n = 6$.[12]

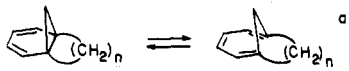
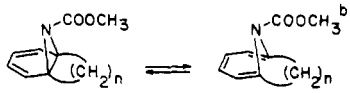
The present investigation relates to semibullvalenes of general structure **1** and was prompted in the main by three considerations. Firstly, the recognized sensitivity of the semibullvalene nucleus to substituent influences[6,8] was expected to reflect itself in rather delicate responses to bracketing effects. Also, because of the doubly degenerate nature of the semibullvalene Cope rearrangement, a *cis*-divinylcyclopropane moiety is retained in both **1a** and **1b.** Consequently, there exists no heavily weighted ground state preference for one of the constituent isomers as is the case with the isomer pairs in Table I, and wide variations in strain are no longer the necessarily dominant issue. It seemingly follows from *a priori* considerations that the various aliphatic chains would affect the position of equilibrium chiefly by inductive stabilization. If those factors which would tend to stabilize the central cyclopropane ring in **1b** are ignored, then experiment[6,8] and theory[4,5] suggest that **1a** should be favored provided that the "belt" is sufficiently "loose." As will be shown herein, this is an oversimplified analysis of the actual situation, the annulation effects operating in **1** not paralleling the general pattern of equilibrium imbalances summarized in Table I. Lastly, because bracketing as in **1** results in symmetrical substitution of the semibullvalene ring system, evaluation of the substituent parameters can be made without concern for contributions arising from potentially complicating unsymmetrical perturbational effects.



1a 1b

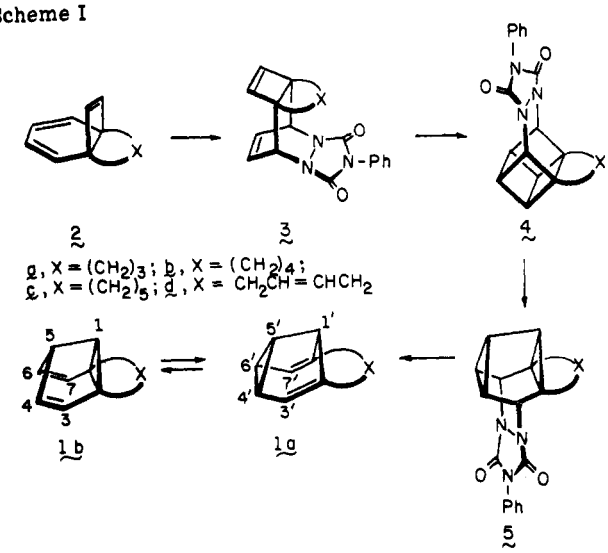
Synthetic Aspects.[13] The starting point for the synthetic plan was the observation that propellatrienes of type **2** undergo Diels–Alder reaction with *N*-phenyltriazolinedione exclusively from the endo face (as drawn) to give adducts **3** in high yield (Scheme I).[14] The preparation of propellatrienes **2b** and **c** has been elaborated earlier,[11] while that of **2a,** which follows an identical course, is summarized in Scheme II. Access to **2d** was gained by monobromination of [4.4.2]propella-3,8,11-triene with pyridinium hydrobromide perbromide and subsequent bis-dehydrobromination with dry lithium chloride and lithium carbonate in anhydrous hexamethylphosphoramide. Proof of the stereochemistry of adducts **3** was available in the form of their ready sensitized (acetone) photocyclization to the diazacubanes **4.** The characterization of **4** rests upon pmr data which are particularly diagnostic of the inherent symmetrical features (see Experimental Section) and the susceptibility of these molecules to Ag^+-catalyzed skeletal rearrangement.[15,16] Recourse was made to somewhat varied conditions in an effort to realize maximum yields of the diazasnoutanes. Silver perchlorate in refluxing benzene was effective in promoting bond relocation in **4a** and **d** with formation of **5a** and **d** in yields of 86 and 89%, respectively. The reaction times were

Table I. Ground-State Equilibrium Effects in Annulated Polyunsaturated Molecules

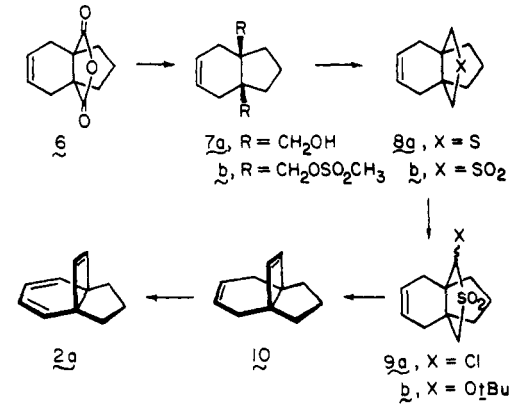
Ring system	Bridge size $n = 3$	$n = 4$	$n = 5$	$n = 6$
 [a]	Tricyclic	Bicyclic		
 [b]	Tricyclic	Bicyclic		
 [c]	Tricyclic	Tricyclic	Bicyclic	
 [d]	Tricyclic	Tricyclic	Tricyclic	Bicyclic

[a] See ref 9 and 10. [b] L. A. Paquette, D. E. Kuhla, J. H. Barrett, and R. J. Haluska, *J. Org. Chem.*, **34**, 2866 (1969). [c] See ref 11. [d] See ref 12.

Scheme I



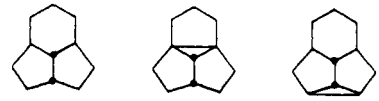
Scheme II



significantly different; however, isomerization of **4d** required approximately 60 hr for completion and that of **4a** necessitated 108 hr. Efficient (88%) production of **5b** in a reasonable time frame was achieved in methanol–water (4:1) as solvent and a reflux period of 48 hr. Neither set of conditions was applicable to the synthesis of **5c;** however, utilization of isopropyl alcohol–water (4:1) led to a 66% yield of this saturated snoutane after 16 days at the reflux temperature. The four cyclopropyl protons in each of the diazasnoutanes appear in the pmr spectra substantially upfield shifted from the cyclobutyl protons in their cubyl counterparts, a feature which proved to be of practical value for the initial qualitative assessment of the individual rearrangement rates.

Hydrolysis of **5a** and **c** and subsequent oxidation (with concomitant loss of nitrogen) were successfully realized by initial heating with potassium hydroxide in isopropyl alcohol at 100° under oxygen-free conditions, acidification to pH 2 with 3 *N* hydrochloric acid, readjustment of the pH after 5 min at 0° to the mildly alkaline side with 3 *N* aqueous ammonia, and exposure to activated manganese dioxide. With **5b** and **d,** utilization of these milder conditions did not prove necessary and direct vigorous alkaline hydrolysis to the hydrazo compound followed by air oxidation gave the desired hydrocarbons. Purification in each case was achieved by preparative vpc methods on short columns.

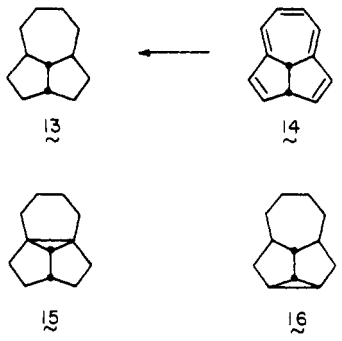
The pmr and cmr features of the annulated semibullvalenes are discussed in the following section. Confirmation of the gross structural features was achieved in two examples by catalytic hydrogenation. Under conditions where an anhydrous tetrahydrofuran solution of the trimethylene derivative was treated with 5% rhodium on carbon and hydrogen at atmospheric pressure, two hydrocarbons were isolated in a 4:1 ratio. The major product, a $C_{11}H_{18}$ compound on the basis of elemental and mass spectral data, was identical in melting point, infrared absorptions, and vpc retention times with an authentic sample of perhydrocyclopent[*cd*]indene (**11**).[17] The less predominant substance proved to be $C_{11}H_{16}$ in nature and was tentatively assigned structure **12a** and/or **12b** on the basis of its pmr spectrum (see Experimental Section).[18]



Comparable treatment of the tetramethylene homolog led to the isolation of **13** (36%) and a nonseparated mixture of **15** and **16** (16%). An authentic sample of perhydro derivative **13** was available from the catalytic hydrogenation of pentaene **14.**[13,19]

In characteristic fashion,[18,20] all of the annulated semibullvalenes exhibit relatively weak ultraviolet spectra (isooctane solution) in the form of a shoulder on the fringe of intense end absorption. The trimethylene bridged derivative proved to be the most susceptible to polymerization, complete decomposition occurring within hours upon its exposure to the atmosphere at ambient temperature.

Pmr and Cmr Spectra.[13,21] With the successful synthesis of several representative members of the **1a** ⇄ **1b** series, attention was directed to an evaluation of the changes in equi-



librium position which accompany structural modification of the bracketing unit. Since the pentamethylene derivative was found to exist as a near equal distribution of valence isomers at room temperature and to exhibit a strong temperature dependence of the equilibrium constant, this hydrocarbon readily accommodated variable-temperature pmr studies and was the first to be investigated in detail. Under conditions of fast exchange (+40°) in deuteriochloroform, the pmr spectrum consists of a doublet at δ 4.98 arising from the permanently olefinic protons H_3,H_7, an equilibrium-diagnostic multiplet centered at δ 3.75 due to H_4,H_6, a second multiplet at δ 3.00 attributable to H_5, and a doublet at δ 2.78 provided by H_1. The equilibrium-dependent allylic protons of the bracket (area 4) appear at δ 2.38–2.65 and the remaining six methylene protons are responsible for the envelope at δ 1.40–2.10. Two sets of low-temperature experiments were carried out. The first, undertaken with the collaboration of Lambert and Greifenstein,[21a] was conducted at 90 MHz in CF_2Cl_2–CD_2Cl_2 over the range −27 to −120°. Gradual cooling of the sample resulted initially in retardation of the rate of Cope rearrangement to that of the pmr time scale and ultimately down to the slow-exchange level where direct spectral observation of two nondegenerate semibullvalene isomers proved possible for the first time. The large structural difference between H_4,H_6 and H_4',H_6' causes their average resonance to broaden at −51°, pass through coalescence at −85.5°, and then separate into two distinct peaks at −120° with the olefinic pair of **1b** appearing at δ 5.59 and the cyclopropyl pair of **1a** at δ 2.34. The permanently olefinic protons of the two valence isomers likewise give separate slow-exchange peaks at δ 5.19 (H_3,H_7) and 4.94 (H_3',H_7'). Complete proton assignment at the lowest temperature clearly showed the more populous isomer to be **1b.** Integration of the H_3,H_7 and H_3',H_7' peaks denoted that at −120° there exists 84% of **1b** and 16% of **1a,** corresponding to a $\Delta G°$ of 505 cal/mol. Given the slow-exchange chemical shifts of H_4,H_6 and H_4',H_6' ($\Delta\nu$ = 290.6 Hz) and the isomer populations, the free energy of activation was determined by complete lineshape analysis at the coalescence temperature to be 8.9 kcal/mol (**1b** to **1a**) or 8.5 kcal/mol (**1a** to **1b**).

These ΔG^* values for Cope rearrangement are larger than that determined experimentally for octamethylsemibullvalene (6.5 kcal/mol at −141°)[3] or estimated from theoretical consideration for semibullvalene itself (2.3–3.3 kcal/mol)[5] and are more closely aligned in magnitude to the ΔG^*'s found for the degenerate rearrangements of barbaralane (7.8 kcal/mol at −77°),[22] 9-methylenebarbaralane (9.5 kcal/mol at −89.5°),[23] dihydrobullvalene (9.5 kcal/mol at −40°),[24] and barbaralone (10.5 kcal/mol at −41°).[23,25] Thus, the energy advantage which is normally acquired in such systems by shortening of the bridge between C_1 and C_5 to the point where these atoms are directly bonded is offset to some degree by the presence of the pentamethylene bracket which joins C_2 to C_8.

The results of a comparable study in CF_2Cl_2–CD_2Cl_2–TMS (1:1:1) solution at 100 MHz within the temperature limits −30.1 and −84.8° are summarized in Table II. The mole fraction of **1b** and the K_{eq} value at each temperature were computed on the basis of the equations

Table II. Low-Temperature Pmr Data [100 MHz, CF_2Cl_2–CD_2Cl_2–TMS (1:1:1)], Computed Equilibrium Constants (K_{eq}), and Gibbs Free Energy Values ($\Delta G°$) for the Fluxional System **1a** ⇄ **1b** [X = $(CH_2)_5$]

Temp, °C	Chemical shift, H_4,H_6, δ	Mol fraction of **1b**	K_{eq}, **1a**/**1b**	Ln K_{eq}	$\Delta G°$, cal/mol
−30.1	4.26	59.1	0.692	−0.368	178
−45.2	4.40	63.4	0.577	−0.550	249
−54.3	4.47	65.5	0.527	−0.641	279
−66.3	4.56	68.3	0.464	−0.768	315
−71.8	4.61	69.8	0.433	−0.837	335
−74.8	4.66	71.4	0.401	−0.914	360
−78.8	4.69	72.3	0.383	−0.960	370
−81.8	4.72	73.2	0.366	−1.005	382
−84.8	4.76	74.5	0.342	−1.073	401

$$\delta_m = p\delta_v + (1 - p)\delta_c$$
$$p = (\delta_m - \delta_c)/(\delta_v - \delta_c) \quad (1)$$
$$K_{eq} = p/(1 - p)$$

where δ_m is the observed chemical shift of that pair of protons undergoing rapid exchange between H_4,H_6 and H_4',H_6' sites at the given temperature, δ_v and δ_c are the chemical shifts of H_4,H_6 and H_4',H_6', respectively, at their slow-exchange limits (−120°), and p is the mole fraction of one of the isomers (**1b** in this instance).[6,26] The enthalpy ($\Delta H°$ = 1130 cal/mol) and entropy ($\Delta S°$ = +3.9 eu) of this semibullvalene system were obtained from the data in Table II by plotting ln K_{eq} *vs.* $1/T$ and deriving by the method of least-squares the slope ($-\Delta H°/R$) and intercept ($\Delta S°/R$) values.

When eq 1 was applied to the 40° pmr spectra (60 MHz) of all four annulated semibullvalenes in deuteriochloroform solution, the approximate[27] mole fraction and $\Delta G°_{313}$ terms of the series for that temperature became readily accessible. These data are collected in Table III for the purpose of direct comparison. Thereby revealed is the fact that 2,8-pentamethylene bridging acts on the energy of the semibullvalene moiety to favor form **1b** at low temperature, but to crossover and stabilize valence isomer **1a** in the vicinity of 17° and above. It is therefore obvious from these findings that the assumedly lesser bracketing strain in this hydrocarbon is not exploited in a manner such as to reveal itself by excessive weighting in the **1a** direction throughout the tem-

Table III. Pmr Data (60 MHz, $CDCl_3$), Computed Equilibrium Constants (K_{eq}), and Gibbs Free Energy Values ($\Delta G°$) for the Annulated Semibullvalenes (40°)

X	Chemical shift, H_4,H_6, δ	Mol fraction of **1b**	K_{eq}, **1a**/**1b**	$\Delta G°$, cal/mol
$(CH_2)_3$	4.21	57	0.75	175
$(CH_2)_4$	2.70	10	9.00	−1360
$(CH_2)_5$	3.75	42	1.38	−200
$CH_2CH{=}CHCH_2$	4.74	74	0.35	650

perature span examined. In striking contrast, those congeners in which X = $(CH_2)_4$ and $-CH_2CH{=}CHCH_2-$ are characterized by K_{eq}'s which are rather heavily weighted in mutually opposite directions, only the tetramethylene derivative conforming to the established preference of alkyl groups for bonding to sp^2- rather than $sp^{2.25}$-hybridized carbon in structurally related homotropilidene systems.[6,28,29] These last two examples expectedly exhibit temperature-dependent pmr behavior but of a very weak order. Consequently, further changes in ground-state equilibria with changing T were too small to measure accurately.

This same difficulty persisted in the trimethylene system but to a somewhat attenuated degree. Its pmr spectrum (40°) is characterized by a 2:2:2:4:2 ratio of protons, the relevant chemical shifts of which correspond closely to those of semibullvalene.[30] Accordingly, a more equal distribution of the two valence isomers exists in this instance at this temperature (see Table III). Variable-temperature studies in carbon disulfide solution from +45 to −91° likewise revealed a crossover in the preferred direction of equilibrium but in the reverse sense from that of the pentamethylene case and to a less dramatic extent (Table IV). Here the $\Delta H°$ value was −315 cal/mol, with $\Delta S°$ equal to −1.29 eu.

Table IV. Low-Temperature Pmr Data (60 MHz, CS_2), Computed Equilibrium Constants (K_{eq}), and Gibbs Free Energy Values ($\Delta G°$) for the Fluxional System **1a** ⇄ **1b** [X = $(CH_2)_3$]

Temp, °C	Chemical shift, H_4,H_6, δ	Mol fraction of **1b**	K_{eq}, **1a**/**1b**	Ln K_{eq}	$\Delta G°$, cal/mol
+45	4.08	53.5	0.869	−0.140	88
−29	3.96	49.8	1.00	0.000	0
−56	3.92	48.6	1.06	0.058	−25
−91	3.77	44.0	1.27	0.239	−86

The valence isomeric equilibria of semibullvalene and several of the annulated derivatives have also been investigated by cmr spectroscopy. In collaboration with Professor E. Wenkert and E. Hagaman, the spectra were recorded at room temperature and all chemical shifts assigned as summarized in Table V.[21b] The properties of the parent hydrocarbon which comprise only three widely spaced signals are fully reconcilable with a rapidly equilibrating pair of degenerate isomers. With these chemical shifts as guidelines, those of the tetramethylene bridged system are seen to be characterized by a high-field position for H_4,H_6 and a low-field position for H_2,H_8. The central carbon atoms must therefore be less cyclopropanoid and the peripheral carbons less olefinic on a time-averaged basis than the respective centers in semibullvalene. As one progresses downward in Table V, this trend is seen to reverse itself. These shift considerations confirm the earlier conclusions derived from pmr studies that the tautomer disposition of the tetramethylene bridged semibullvalene lies heavily in the **1a** direction, that of the $-CH_2CH{=}CHCH_2-$ example shifted appreciably toward **1b**, and that of the pentamethylene case at an intermediate position.

Discussion

A reliable value for the equilibrium imbalance arising from alkyl substitution of the semibullvalene ring at C_2 is extractable from the behavior of the 2(4)-methyl derivative.[6] Here the methyl group, which is almost certainly electron releasing relative to hydrogen,[31] is seen to exert an electrical effect within the molecule which alters the relative potential energies in such a way as to favor **17a** by approximately 1 kcal/mol at 40°. In this instance, the free energy difference lies in the expected direction.[6,28,29] Placement of a second methyl group at C_8 should approximately double the value of $\Delta G°$, barring unforeseen steric problems of meaningful magnitude. Extrapolation of this analysis to an annulated semibullvalene of type **1a** ⇄ **1b** in which the "belt" is not excessively truncated predicts that valence tautomer **1a** should be highly (>95%) favored if all other factors are equal.

17a 17b

However, the fact that alkyl chains are "mobile substituents"[32] must be reckoned with. This means that intramethylene rotations of the side chain about the bond connecting it to the host molecular framework, in tandem with steric crowding, strain factors, and electronic demand, have a direct effect on the internal mobility of the molecule. In other words, the particular characteristics of a given alkyl chain can greatly affect its overall contribution to entropy.

The tetramethylene example, X = $(CH_2)_4$, is an interesting case in point. At 40° in $CDCl_3$, isomer **1a** is seen to be present to the extent of approximately 90%. Additionally, its pmr spectra are weakly temperature-dependent, a finding which signifies that $\Delta H°$ approaches zero, and consequently $\Delta G° \approx -T\Delta S°$ (see Table VI). Entropy control prevails throughout the entire temperature range examined, and **1a** convincingly dominates the equilibrium, likely because it has access to a wider variety of translational, rotational, and vibrational motions (or conformations) than does **1b**. However, the four methylene groups seemingly do

Table V. Summary of Cmr Data (15.08 MHz, $CDCl_3$, Ambient Temperature)

Compd	Chemical shifts, δ[a] C_1	C_2,C_8	C_3,C_7	C_4,C_6	C_5	α[b]	β[b]	δ[b]
Semibullvalene	50.0	86.5	120.4	86.5	50.0			
1a ⇄ **1b**, X = $(CH_2)_4$	56.4[c]	145.7	115.5	41.3	48.1[c]	30.3	26.2	
1a ⇄ **1b**, X = $(CH_2)_5$	59.6[c]	109.1	121.4	82.2	52.4[c]	30.0	28.0	29.0
1a ⇄ **1b**, X = $(-CH_2CH{=})_2$	55.0[c]	83.1	122.4	101.0	53.0[c]	28.6	124.1	

[a] In ppm downfield from TMS. [b] Relates to the carbon atoms of the bracket with the α position being most proximal to the semibullvalene nucleus. [c] These values may be interchanged.

Table VI. Summary of Thermodynamic Data for the **1a** ⇄ **1b** Equilibria

X	Change in ring size	$\Delta H°$, kcal/mol	$\Delta S°$, eu
$(CH_2)_3$	6 → 5	+0.3	+1.3
$(CH_2)_4$	7 → 6	~0	~−4.4
$(CH_2)_5$	8 → 7	−1.13	−3.9
$CH_2CH{=}CHCH_2$	7′ → 6′	~0	~+2.1

introduce some strain relative to the hypothetical 2,8-dimethylsemibullvalene model such that the concentration of **1a** is energetically precluded from exceeding the 90% level at 40°.

Introduction of a double bond into this four-carbon sidechain to give the molecule where X = $CH_2CH{=}CHCH_2$ generates significant amounts of added strain and molecular constraint so as now to favor isomer **1b.** The enthalpy term again gives indication of being small in magnitude such that entropy control again prevails. But the marked perturbation of the translation, rotation, and vibration transitions resulting from introduction of the additional π bond causes **1b** with its 3-norcarene part structure to possess the greater level of conformational freedom. Accordingly, an equilibrium crossover relative to the saturated counterpart results.

Enthalpy and entropy increments are sufficiently independent that they sometimes exhibit the same sign and sometimes opposite signs. The above two examples illustrate that combination of effects in which $\Delta H°$ and $T\Delta S°$ may be of opposite sign but with the $T\Delta S°$ term large such that entropy-controlled effects are encountered. In contrast, the trimethylene and pentamethylene systems are observed to possess compensating effects in which the two terms oppose each other but become essentially equal at a given temperature. For the $(CH_2)_3$ derivative (in CS_2), this 50:50 equilibrium point is attained at −29°, while for the $(CH_2)_5$ congener (in CF_2Cl_2–CD_2Cl_2) the extrapolated temperature is +17°. As expected, therefore, moderate variations from these temperatures serve to convert effects that are slightly enthalpy controlled into those that are slightly entropy controlled. Both hydrocarbons exhibit these characteristics; interestingly, however, they do so in opposite directions.

At higher temperatures, the trimethylene bridged system preferentially adopts conformation **1b** because of swamping out of the $\Delta H°$ term by the $T\Delta S°$ term. The prevalence of **1b** is compatible with the notion that this isomer possesses the greater degree of conformational freedom.[33] This preferential weighting in favor of that valence tautomer in which the cyclopropane ring occupies a position central to the two larger rings has its origins chiefly[33] in the molecular constraint differences between a trisubstituted bicyclo[3.1.0]hexane moiety (**1b**) and a rigidly fixed 1,3-dimethylenecyclohexane part structure (**1a**).[33] The application of Benson and O'Neal's group additivity criterion for estimating gas-phase entropies[34] to such complex species as these could prove interesting if few approximations were involved. The preference for **1a** when enthalpy control takes over (below −29°) can be understood on the basis of recognized preferred alkyl attachment to trigonal centers.[6,28,29]

Expansion of the bridge to five methylene carbons generates a situation where entropic differences between the two valence isomers are maximized to a yet greater extent. But because the enthalpy term is also large, the change in $\Delta G°$ is less than would be expected on the basis of either $\Delta H°$ or $T\Delta S°$ alone. This is an example where $\Delta H°$ and $\Delta S°$ vary in a compensating manner, the large change in enthalpy being accompanied by a large change in the temperature–entropy term. This phenomenon has earlier been referred to by Leffler[35] as an isoequilibrium relationship. At the lower temperatures where enthalpy control operates, isomer **1b,** X = $(CH_2)_5$, is favored, presumably as the result of more favorable bond strength contributions. However, the true causative factors underlying the preferential attachment of the α-methylene groups to $sp^{2.25}$- rather than sp^2-hybridized carbon in this instance remain elusive. With heating, entropy control sets in, and **1a** becomes dominant as a likely consequence of a higher level of strain (from nonbonded interactions and the like) in the various conformations available to **1b.**[33]

In summary, we are of the opinion that the varied ground-state behavior of the annulated semibullvalenes provides an unusually clear example of the caution which must be exercised in equating a diminution in "bracketing strain" with direction of equilibrium. Earlier studies of this phenomenon (Table I) have uniformly succeeded in their predictability, *i.e.,* in equating favored bicyclic character with an increase in bridge size, because of the unusually large equilibrium displacements toward the minimum number of ring constraints which already exist in the parent nonbridged systems.[36] However, when a twofold degenerate host molecule such as semibullvalene is involved, similar unidirectionally weighted equilibrium imbalances are not present, and the quite subtle libration effects of the various aliphatic chains which comprise the bracket are consequently revealed.

Experimental Section

Melting points are corrected and boiling points are uncorrected. Proton magnetic resonance spectra were obtained on Varian A-60 A, Varian HA-100, and Jeolco MH-100 spectrometers; apparent splittings are given in all cases. Infrared spectra were determined on Perkin-Elmer Model 137 and 467 instruments. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionizing potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

7,9-Dioxo-8-oxa[4.3.3]propell-3-ene (6). To a stirred solution of ethyl cyclopentanone-2-carboxylate (117 g, 0.750 mol) in 250 ml of ether was added 146 g (2.25 mol) of potassium cyanide. After the mixture had been cooled in an ice bath, 207 ml (2.25 mol) of concentrated hydrochloric acid was added over a period of 1 hr under nitrogen, and stirring was maintained for 1 hr at 0° and for 14 hr at ambient temperature. After the residual hydrogen cyanide had been removed by entrainment with nitrogen, the yellow organic layer was separated, and the aqueous phase was washed with ether (3 × 150 ml). The combined organic layers were washed with sodium carbonate solution, water, and brine. After drying and ether removal, the crude cyanohydrin was dissolved in 178 g of cold pyridine and treated with 268 g (2.25 mol) of thionyl chloride during 1 hr at 0° under nitrogen. After the solution had been stirred at room temperature for 12 hr, it was carefully poured into 3 l. of ice and water and extracted with ether (6 × 200 ml). After processing as above, the residual oil was distilled to give 112.8 g (91%) of ethyl 1-cyanocyclopentene-2-carboxylate, bp 84–85° (0.5 mm) [lit.[37] bp 132° (11 mm)]: ν_{max} (neat) 2950, 2225, 1725, 1220, and 764 cm^{-1}.

A 60.0-g sample (0.364 mol) of this cyano ester was added to 100 ml of concentrated hydrochloric acid, and the resulting mixture was refluxed with stirring for 2 hr. Water (100 ml) was introduced, and reflux was resumed for an additional 2.5 hr. The diacid was collected by filtration and dried over potassium hydroxide at 0.1 mm. There was obtained 49.0 g (86.4%) of cyclopentene-1,2-dicarboxylic acid, mp 174.5–176.5° (lit.[38] mp 178°): δ_{DSS} (D_2O) 2.88 (t, J = 7 Hz, 4, allylic) and 1.94 (m, 2, methylene).

A solution of 78 g (0.5 mol) of the diacid in 200 ml of acetic anhydride was heated at reflux with stirring for 4 hr. After cooling, the solution was removed by distillation at 10 mm, and the residue was subsequently fractionated to give 64.2 g (93.0%) of the white crystalline anhydride, bp 92–94° (0.3 mm), mp 178–180° (lit.[38] bp 130° (5 mm)]: ν_{max} ($CHCl_3$) 3000, 1850, 1775, 1670, 1320, 1085, and 874 cm^{-1}.

A mixture of 27.6 g (0.20 mol) of cyclopentene-1,2-dicarboxylic anhydride, 20 ml of dioxane, and 147 g (2.73 mol) of butadiene was heated in a heavy wall sealed glass vessel at 120° for 12 hr. The cooled reaction mixture was evaporated to remove the volatiles, and the residue was crystallized from chloroform–hexane to furnish 35.5 g (92.1%) of **6,** mp 117–118° (lit.[39] mp 122° from hexane): ν_{max} ($CHCl_3$) 2950, 1850, 1790, 1450, and 970 cm^{-1}; ν_{TMS} ($CDCl_3$) 6.04 (pent, J = 1.8 Hz, 2, olefinic) and 1.68–3.00 (br m, 10, allyl and methylenes).

cis-**1,6-Bis(hydroxymethyl)bicyclo[4.3.0]non-3-ene (7a).** To a

slurry of 38 g (1 mol) of lithium aluminum hydride in 1.5 l. of anhydrous tetrahydrofuran was added dropwise under nitrogen a solution of **6** (129 g, 0.667 mol) in 1 l. of the same solvent, and the mixture was refluxed for 6 hr. With ice cooling, 38 g of water, 38 ml of 30% sodium hydroxide solution, 114 ml of water, and 5 g of anhydrous magnesium sulfate were added sequentially. The inorganic salts were filtered and twice leached with 500 ml of refluxing ether. The combined organic layers were dried and evaporated, and the residue was recrystallized from chloroform–hexane to give 114.2 g (94.0%) of **7a**, mp 173–177° (lit.[39] mp 158–160° from hexane): ν_{max} ($CHCl_3$) 3400, 2960, 1065, and 1030 cm^{-1}; δ_{TMS} ($CDCl_3$) 5.59 (m, 2, olefinic), 4.53 (s, 2, –OH), 3.52 (AB q, J_{AB} = 12.2 Hz, $\Delta\nu_{AB}$ = 8.2 Hz, 4, $-CH_2O-$), 2.03 (m, 4, allyl), and 1.63 (br s, 6, methylenes).

cis-**1,6-Bis(methanesulfonyloxymethyl)bicyclo[4.3.0]non-3-ene (7b).** A mechanically stirred solution of 230 g (2.0 mol) of methanesulfonyl chloride in 1 l. of cold pyridine was treated dropwise with a solution of **7a** (117.2 g, 0.644 mol) in 500 ml of the same solvent. After being stirred at −5° for 3.5 hr, the mixture was treated with sufficient ice to destroy the excess sulfonyl chloride, and 10% hydrochloric acid was added until distinctly acidic. The solution was allowed to stand at 0° for 1 hr, whereupon the precipitate was filtered, washed with cold water, and dried *in vacuo* over phosphorus pentoxide. There was obtained 218 g (100%) of **7b**, mp 74.0–74.5° (from chloroform–hexane): ν_{max} ($CHCl_3$) 2950, 1650, 1450, 1340, 1160, and 940 cm^{-1}; δ_{TMS} ($CDCl_3$) 5.65 (m, 2, olefinic), 4.13 (s, 4, $-CH_2O-$), 3.00 (s, 6, methyl), 2.13 (br s, 4, allyl), and 1.77 (br s, 6, methylene).

Anal. Calcd for $C_{13}H_{22}O_6S_2$: C, 46.11; H, 6.55; S, 18.91. Found: C, 46.17; H, 6.75; S, 18.75.

8-Thia[4.3.3]propell-3-ene (8a). Into a 2-l. three-necked flask fitted with a mechanical stirrer and distillation head were placed 98.2 g (0.93 mol) of freshly recrystallized (ethanol) sodium sulfide nonahydrate and 500 ml of anhydrous hexamethylphosphoramide (HMPA). Dehydration was achieved by distillation of the HMPA at 15 mm until the temperature of the distillate reached 135°. The dull blue colored solution was cooled to 40°, 105.6 g (0.313 mol) of **7b** was added, and the mixture was heated at 120° with stirring for 18 hr. It was subsequently cooled in ice, diluted with 500 ml of water, and extracted with pentane (5 × 300 ml). The combined organic layers were washed with water (6 × 200 ml) and brine, dried, and evaporated. The viscous red liquid was redissolved in pentane (1 l.) and the solution passed through a column of neutral activity I alumina. Evaporation of the eluate afforded 53.7 g (95.4%) of **8a** as a white solid, mp 88–92°: ν_{max} ($CHCl_3$) 2950, 1645, 1450, 1435, 1420, and 1120 cm^{-1}; δ_{TMS} ($CDCl_3$) 5.63 (t, J = 1.8 Hz, 2, olefinic), 2.78 (AB q, J_{AB} = 11 Hz, $\Delta\nu_{AB}$ = 6.9 Hz, 4, $-CH_2S-$), 2.12 (m, 4, allyl), and 1.75 (m, 6, methylenes).

Oxidation of a small sample of this sulfide with 2 equiv of *m*-chloroperbenzoic acid afforded the more crystalline sulfone **8b**, mp 136.5–137.5° (from hexane): ν_{max} ($CHCl_3$) 2900, 1670, 1410, 1290, 1130, and 1110 cm^{-1}; δ_{TMS} ($CDCl_3$) 5.76 (t, J = 2.4 Hz, 2, olefinic), 3.07 (s, 4, $-CH_2SO_2-$), 2.23 (br s, 4, allyl), and 1.86 (br s, 6, methylenes).

Anal. Calcd for $C_{11}H_{16}O_2S$: C, 62.61; H, 7.60; S, 15.11. Found: C, 62.38; H, 7.68; S, 15.04.

7-Chloro-8-thia[4.3.3]propell-3-ene 8,8-Dioxide (9a). To a solution of 8.2 g (45.6 mmol) of **8a** in 50 ml of carbon tetrachloride chilled to 0° was slowly added 6.4 g (47.8 mmol) of *N*-chlorosuccinimide. The mixture was refluxed for 6 hr, cooled, filtered, and evaporated. The residual α-chloro sulfide was dissolved in 100 ml of ether and cooled to 0°. To this stirred solution was added dropwise a standardized ethereal solution containing 95.6 mmol of monoperphthalic acid, and stirring at room temperature was maintained for 12 hr. The precipitated phthalic acid was removed by filtration, and the filtrate was washed with 0.5 *N* sodium hydroxide solution, water, and brine, dried, and evaporated. There remained 10.9 g (97.7%) of **9a** as a white solid, mp 107–117°. Integration of the >CHCl absorptions of the isomeric pair of α-chloro sulfones (δ 4.83 and 4.73) revealed the isomer distribution to be 39:61.

The major isomer, assigned the configuration with chlorine syn to the cyclopentane ring by analogy,[40] was obtained in pure form by elution chromatography on silica gel (ether–petroleum ether mixtures), mp 126–128° (from hexane): δ_{TMS} ($CDCl_3$) 5.76 (m, 2, olefinic), 4.68 (s, 1, >CHCl), 3.05 (br s, 2, $-CH_2SO_2-$), and 1.53–2.31 (br m, 10, allylic and methylenes).

Anal. Calcd for $C_{11}H_{15}ClO_2S$: C, 53.52; H, 6.13; S, 13.00. Found: C, 53.60; H, 6.12; S, 12.88.

[4.3.2]Propella-3,10-diene (10). To an ice-cold magnetically stirred solution of 5.0 g (20.3 mmol) of **9a** in 175 ml of anhydrous tetrahydrofuran was added 9.9 g (88.3 mmol) of commercial powdered potassium *tert*-butoxide in one portion. The mixture was stirred at room temperature for 1 hr, heated at reflux for 3 hr, cooled in ice, and treated with water. Extraction with pentane, followed by washing of the combined organic layers with water and brine, drying, and careful solvent removal by distillation at atmospheric pressure through a 6-in. metal helix-packed column gave a residual oil. If this material was subjected to distillation at reduced pressure, 1.25 g (41%) of **10**, bp 67° (10 mm), was obtained: ν_{max} (neat) 3040, 2930, 1650, 1450, 1095, 975, 883, 825, and 755 cm^{-1}; δ_{TMS} ($CDCl_3$) 5.72 (m, 4, olefinic), 0.9–2.47 (continuous series of multiplets, 10, allylic and saturated methylenes).

Anal. Calcd for $C_{11}H_{14}$: C, 90.34; H, 9.66. Found: C, 90.28; H, 9.60.

If the oil is subjected to chromatography on silica gel instead, there can be isolated in addition to **10**, the α-*tert*-butoxy sulfone **9b**, mp 76–77° (from hexane): ν_{max} ($CHCl_3$) 2950, 1475, 1375, 1300, 1155, 1090, and 883 cm^{-1}; δ_{TMS} ($CDCl_3$) 5.61 (m, 2, olefinic), 4.52 (s, 1, >CHO–), 3.04 (AB q, J_{AB} = 13 Hz, $\Delta\nu_{AB}$ = 7.5 Hz, 2, $-CH_2SO_2-$), 1.84–2.30 (br m, 10, allylic and saturated methylenes), and 1.31 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{15}H_{24}O_3S$: C, 63.32; H, 8.51; S, 11.28. Found: C, 63.22; H, 8.56; S, 11.37.

[4.3.2]Propella-2,4,10-triene (2a). Pyridinium hydrobromide perbromide (3.90 g, 12.2 mmol) was added in one portion to a magnetically stirred solution of 1.62 g (11.1 mmol) of **10** in 30 ml of carbon tetrachloride–acetic acid (1:1), and the mixture was stirred at room temperature with protection from the atmosphere for 12 hr. The reaction mixture was diluted with ether and washed sequentially with water, 0.5 *N* sodium hydroxide solution, saturated sodium bicarbonate solution, water, 10% sodium thiosulfate solution, water, and brine. Drying and solvent removal *in vacuo* (no heat) left 2.86 g (87%) of dibromide as a viscous pale reddish oil which was used without further purification.

A solution of 10.24 g (33.5 mmol) of this dibromide in 300 ml of dry hexamethylphosphoramide was treated with 28.2 g (0.664 mol) of anhydrous lithium chloride (both lithium salts were dried over phosphorus pentoxide *in vacuo* before use) and 35.6 g (0.482 mol) of anhydrous lithium carbonate, and the slurry was heated at 95–100° with magnetic stirring under nitrogen for 25 hr. After cooling, the slurry was diluted with water and extracted with pentane. The combined organic layers were washed with water and brine, dried, and passed through a neutral activity I alumina column. Careful solvent removal by distillation at atmospheric pressure through a metal helix-packed 6-in. column and removal of the remaining traces of solvent at 20° (20 mm) gave 3.43 g (73%) of **2a**: ν_{max} (neat) 2900, 1445, 1395, 1220, 1095, 949, 763, and 700 cm^{-1}; λ_{max} (cyclohexane) 266 (ε 3380), 231 (1710), and 225 nm (2000); δ_{TMS} ($CDCl_3$) 5.71–5.78 (m, 6, olefinic) and 0.99–1.79 (br m, 6, methylenes).

Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.45; H, 8.54.

***N*-Phenyltriazolinedione Addition to 2a.** A cold (−78°) magnetically stirred solution of **2a** (562 mg, 3.90 mmol) in 50 ml of acetone was treated dropwise with a solution containing 683 mg (3.91 mmol) of *N*-phenyltriazolinedione in 25 ml of acetone. The solution was allowed to warm to room temperature where it was kept for 1 hr and then refluxed until the red color faded. Solvent removal left a yellowish solid which was chromatographed on neutral activity I alumina. Elution with 30% chloroform in ether afforded 1.07 g (86%) of adduct **3a** as a white solid, mp 253.0–253.5° (from acetone–hexane): ν_{max} ($CHCl_3$) 2930, 1770, 1710, 1490, 1400, 1260, 1135, and 1075 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.41 (s, 5, aromatic), 6.24 (t, J = 3.8 Hz, olefinic), 5.86 (s, 2, cyclobutene), 4.87 (br t, J = 3.8 Hz, 2, >CH–N<), and 1.50–2.08 (br m, 6, methylenes).

Anal. Calcd for $C_{19}H_{17}N_3O_2$: C, 71.44; H, 5.37; N, 13.17. Found: C, 71.19; H, 5.36; N, 13.05.

Photocyclization of 3a. A solution of 1.03 g (3.22 mmol) of **3a** in 350 ml of deoxygenated acetone was irradiated under a nitrogen atmosphere with a 200-W Hanovia lamp fitted with a Vycor filter for 2 hr. Solvent evaporation *in vacuo* left a yellow crystalline solid which was chromatographed on neutral activity I alumina. Elution

with 20% chloroform in ether gave 995 mg (92%) of **4a** as a white crystalline solid, mp 203.5–204.5° (from acetone–hexane): ν_{max} ($CHCl_3$) 2990, 1775, 1700, 1510, 1420, 1325, and 1130 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.26–7.70 (br m, 5, aromatic), 4.96 (t, J = 3 Hz, 2, >CH–N<), 3.43–3.71 (br m, 2, methine), 2.91 (br t, J = 3 Hz, 2, methine), and 1.80 (br s, 6, methylene).

Anal. Calcd for $C_{19}H_{17}N_3O_2$: C, 71.44; H, 5.37; N, 13.17. Found: C, 71.31; H, 5.45; N, 13.12.

Ag^+-Catalyzed Rearrangement of 4a. A 1.10-g (3.45 mmol) sample of **4a** was dissolved in 300 ml of 0.2 *N* silver perchlorate–anhydrous benzene solution and the reaction mixture was refluxed with protection from light and atmospheric moisture (N_2 atmosphere) for 108 hr with magnetic stirring. The solvent was removed *in vacuo*, and the resulting off-white solid was leached with chloroform. The combined filtrates were washed with water and brine, dried, and evaporated. The yellow oil so obtained was triturated with benzene to furnish 948 mg (86%) of **5a** as a white crystalline solid, mp 169.5–170.5° (from ether–hexane): ν_{max} ($CHCl_3$) 2950, 1775, 1700, 1500, 1410, and 918 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.24–7.68 (br m, 5, aromatic), 4.96–5.11 (m, 2, >CH–N<), 1.88–2.04 (m, 6, methylene), and 1.38–1.82 (br m, 4, cyclopropyl).

Anal. Calcd for $C_{19}H_{17}N_3O_2$: C, 71.44; H, 5.37; N, 13.17. Found: C, 71.08; H, 5.46; N, 13.44.

2,8-Trimethylenesemibullvalene. Tetracyclo[5.3.1.$0^{1,7}$.$0^{4,11}$]undeca-2,5-diene [1a ⇄ 1b, X = $(CH_2)_3$]. A mixture of 1.073 g (3.37 mmol) of **5a**, 2.11 g (32.7 mmol) of potassium hydroxide (86.6%), and 30 ml of 2-propanol was deoxygenated with oxygen-free nitrogen and heated to 100° for 1 hr. Upon cooling to 0°, 3 *N* hydrochloric acid (deoxygenated) was added to pH 2. The resulting violet mixture was stirred for 5 min at which point 3 *N* ammonium hydroxide (deoxygenated) was added at 0° until a pH of 8 was attained. The deep bourbon colored solution was stirred for 5 min, and chloroform (10 ml) together with pentane (30 ml) was added. Activated manganese dioxide (2.24 g, 28.0 mmol) was added in one portion (immediate effervescence), and the mixture was stirred at room temperature for 3 hr. After filtration, the filtrate was washed with water (3 × 50 ml) and brine (60 ml), dried over anhydrous sodium sulfate, and carefully concentrated by distillation through a Vigreux column. Preparative vpc purification on a 4 ft × 0.25 in. 5% SF-96 on Chromosorb G column (70°) afforded 94 mg (19.4%) of the semibullvalene as a colorless liquid: ν_{max} (neat) 2950, 1625, 1450, 1340, 914, 832, and 742 cm^{-1}; δ_{TMS} ($CDCl_3$) 4.99 (m, 2, H_3, H_7), 4.12–4.26 (m, 2, H_4, H_6), 2.73–2.93 (m, 2, bridge protons), and 1.54–2.28 (br m, 6, methylenes). Spin decoupling: saturation of the δ 4.99 signal collapsed the peak at δ 4.12–4.26 to a doublet while double irradiation of the δ 4.12–4.26 signal collapsed the δ 4.99 absorption to a singlet and slightly affected the δ 2.73–2.93 multiplet. λ_{max} (isooctane) 240 sh nm (ϵ 4600). Calcd *m/e* 144.0939, found 144.0941.

Hydrogenation of 2,8-Trimethylenesemibullvalene. A 58.3-mg sample (0.40 mmol) of the semibullvalene dissolved in 100 μl of anhydrous tetrahydrofuran was introduced *via* syringe into a hydrogenation flask containing 10 ml of the same solvent and 150 mg of prereduced 5% rhodium on carbon. Hydrogen uptake was immediate, and after 30 min the catalyst was separated. The filtrate was partitioned between pentane and water, and the organic phase was dried and carefully distilled through a 6-in. Vigreux column to remove solvent. The concentrate was subjected to preparative vpc separation (4 ft × 0.25 in. SF-96 on Chromosorb G, 60°). Two products were isolated, the more rapidly eluted (t_{ret} = 16 min) being characterized as **12:** δ_{TMS} ($CDCl_3$) 2.5 (br m, 1), 1.37–1.93 (br m, 12), and 1.26 (br m, 3); calcd *m/e* 148.1252, observed 148.1249.

The product of longer retention time (27.5 min) was a white solid, mp 49–52° (lit.[17] mp 50°), and was identified as **11** by direct comparison with an authentic sample: ν_{max} ($CHCl_3$) 2940, 1450, and 900 cm^{-1}; δ_{TMS} ($CDCl_3$) 1.52 (br envelope); calcd *m/e* 150.1408, observed 150.1406.

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.90; H, 11.92.

5,6,7,8-Tetrahydro-*N*-phenyl-1,4:4a,8a-diethenophthalazine-2,3(1*H*,4*H*)-dicarboximide (3b). To a magnetically stirred solution of 1.01 g (6.41 mmol) of **2b**[11] in 30 ml of acetone at −78° was added dropwise an acetone solution of *N*-phenyltriazolinedione until a slight red color persisted. The solution was allowed to stir at ambient temperature for 2 hr and gently refluxed until the red color disappeared. The solvent was removed on a rotary evaporator, and the white crystalline residue was chromatographed on alumina. Elution with chloroform–ether (1:9) gave 1.99 g (93.5%) of adduct **3b.** Recrystallization from acetone gave an analytical sample, mp 230.0–232.0°; ν_{max} ($CHCl_3$) 1760, 1710, 1490, and 1400 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.45 (m, 5, aromatic), 6.23 (t, J = 4 Hz, 2, olefinic), 5.95 (s, 2, cyclobutene), 4.63 (t, J = 4 Hz, 2, >CH–N<), and 1.4–2.1 (br m, 8, methylene).

Anal. Calcd for $C_{20}H_{19}N_3O_2$: C, 72.05; H, 5.74; N, 12.60. Found: C, 71.65; H, 5.76; N, 12.32.

Hexahydro-*N*-phenyl-1,5a,2,5-ethanediylidene-5a*H*-cyclobuta[*d*]phthalazine-3,4(1*H*,5*H*)-dicarboximide (4b). A solution of 235 mg (0.706 mmol) of **3b** in 160 ml of deoxygenated acetone was irradiated with a 200-W Hanovia lamp through a Vycor filter for 2 hr. Removal of the solvent, followed by chromatography of the yellowish residue on alumina (elution with 20% chloroform in ether) yielded 233 mg (99.4%) of **4b** as a white crystalline solid. An analytical sample, mp 194.0–196.0°, was obtained as plates from ether–chloroform: ν_{max} ($CHCl_3$) 1750, 1690, 1490, and 1400 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.50 (br m, 5, aromatic), 4.66 (t, J = 3.5 Hz, 2, >CH–N<), 3.58 (m, 2, methine), 2.98 (t, J = 3 Hz, 2, methine), and 1.4–2.0 (m, 8, methylene).

Anal. Calcd for $C_{20}H_{19}N_3O_2$: C, 72.05; H, 5.74; N, 12.60. Found: C, 71.76; H, 5.74; N, 12.47.

Octahydro-*N*-phenyl-1,2a,6a-metheno-1*H*-cyclopropa[*b*]naphthalene-2,7-biimine-8,9-dicarboximide (5b). To a magnetically stirred solution of 4.06 g (12.2 mmol) of **4b** in 250 ml of methanol–water (4:1) was added 30.5 g (0.180 mol) of silver nitrate, and the solution was refluxed in the dark for 48 hr. After dilution with water (350 ml), the solution was extracted with chloroform (2 × 250 ml) and the combined extracts were washed with water and brine and dried. Removal of the solvent gave a yellowish oil which crystallized on standing. Elution of the crude product through an alumina column with chloroform–ether (1:3) gave 3.59 g (88.4%) of **5b** as a white crystalline solid, mp 149.0–150.0° (from ether–chloroform): ν_{max} ($CHCl_3$) 2900, 1760, 1690, 1490, 1400, and 1120 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.30–7.73 (br m, 5, aromatic), 4.88 (br t, J = 2.7 Hz, 2, >CH–N<), 1.67–3.20 (br m, 8, proximate methylenes and cyclopropyl), and 0.92–1.50 (br m, 4, remote methylenes).

Anal. Calcd for $C_{20}H_{19}N_3O_2$: C, 72.05; H, 5.74; N, 12.60. Found: C, 71.99; H, 5.77; N, 12.40.

2,3,4,5,6a,6b,6c,6d-Octahydrocyclohepta[*cd*]cyclopropa[*gh*]-pentalene/2a,5,6,7,8,8b-Hexahydrobenzo[1,3]cyclopropa[1,2,3-*cd*]pentalene [1a ⇄ 1b, X = $(CH_2)_4$]. A stream of oxygen-free nitrogen was bubbled for 30 min into a mixture of 3.55 g (10.6 mmol) of **5b,** 12 g of potassium hydroxide, 100 ml of ethylene glycol, and 100 ml of distilled water contained in a Claisen distilling flask fitted with a condenser and 100-ml receiver. The receiver was cooled in a Dry Ice–acetone bath. With continued nitrogen purging, the flask was heated strongly over a wire gauze with a burner flame until approximately 75 ml of clear distillate was collected in the receiver. The distillate and pot residue were combined and diluted with 300 ml of water. The aqueous solution was extracted with methylene chloride (4 × 200 ml), and the combined extracts were oxygenated for 30 min. The solution was washed with water (4 × 600 ml), saturated with sodium chloride solution, and dried. The solvent was carefully removed under reduced pressure (20–30 mm, *no heat*) to give a dark oily mass which was taken up in pentane. The pentane solution was filtered through a Celite pad and the solvent removed as above to give a pale yellow oil. Preparative vpc (4 ft × 0.25 in. 5% SF-96 on Chromosorb G, 80°) yielded 1.06 g (63.1%) of the semibullvalene as a clear oil: ν_{max} (neat) 3000, 2900, 2810, 1450, 1330, 880, 850, 830, 820, 745, and 735 cm^{-1}; δ_{TMS} ($CDCl_3$) 4.82 (br s, 2, olefinic), 2.56–3.09 (br m, 4, bridgehead and "cyclopropyl" protons), 2.11–2.51 (br m, 4, adjacent methylene), and 1.18–1.78 (br m, 4, remote methylene); λ_{max} (isooctane) 235–250 nm (ϵ 3200), shoulder on end absorption. Calcd: *m/e* 158.1095. Found: 158.1097.

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.66; H, 8.83.

Hydrogenation of 1a ⇄ 1b, X = $(CH_2)_4$. A solution of 44 mg (0.28 mmol) of the tetramethylene bridged semibullvalene in 25 ml of dry ether was reduced at 1 atm of hydrogen with *ca.* 100 mg of 5% rhodium on carbon. Hydrogen uptake began immediately and ceased after 15 min. The catalyst was removed by filtration

through a silica gel column, and the solvent was carefully removed through a metal helix-packed column. Vapor phase chromatographic analysis showed two volatile products to be present. A comparison of vpc retention times indicated that no starting material remained. Preparative vpc (4 ft × 0.25 in. 5% SF-96 on Chromosorb G, 90°) gave 7 mg (16%) of tetrahydro derivatives **15** and **16:** ν_{max} (neat) 2990, 2890, 2820, 1450, 1320, and 940 cm^{-1}; δ_{TMS} ($CDCl_3$) 2.60 (m, 1), 1.7 (m, 7), 1.5 (m, 3), and 1.2 (m, 7). Calcd: *m/e* 162.1408. found: 162.1407.

Anal. Calcd for $C_{17}H_{18}$: C, 88.82; H, 11.18. Found: C, 89.01; H, 11.28.

Hexahydro derivative **13** eluted last (16 mg, 36%) as a clear oil: ν_{max} (neat) 2930, 2860, 1470, 1440, 965, 945, and 880 cm^{-1}; δ_{TMS} ($CDCl_3$) 2.6 (br ill defined peak). Calcd: *m/e* 164.1565. Found: 164.1566.

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.81; H, 12.17.

***N*-Phenyltriazolinedione Addition to 2c.** A solution of 41.5 mg (0.241 mmol) of **2c**[11] in 10 ml of ethyl acetate was treated dropwise at room temperature with a solution containing 42.6 mg (0.243 mmol) of *N*-phenyltriazolinedione in 10 ml of ethyl acetate under nitrogen. After the red solution had been refluxed for 18 hr under nitrogen, 5 ml of ethanol was added, the pale yellow solution was allowed to cool to room temperature, and the solvent was removed *in vacuo*. The yellow oil so obtained was chromatographed on silica gel (elution with methylene chloride) to afford 78.4 mg (94%) of **3c** as a white solid, mp 240.0–241.5° (from methylene chloride–hexane): ν_{max} ($CHCl_3$) 2900, 1770, 1700, 1600, 1260, and 908 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.48 (br s, 5, aromatic), 6.28 (t, J = 4 Hz, 2, olefinic), 5.96 (s, 2, cyclobutene), 4.60 (t, J = 4 Hz, 2, >CH–N<), and 1.50–2.30 (m, 10, methylene).

Anal. Calcd for $C_{21}H_{21}N_3O_2$: C, 72.60; H, 6.09; N, 12.09. Found: C, 72.38; H, 6.07; N, 12.08.

Photocyclization of 3c. A solution of 1.50 g (4.33 mmol) of **3c** in 350 ml of acetone was deaerated with nitrogen and irradiated with a 200-W Hanovia lamp (Vycor filter) for 2 hr. The solvent was removed on a rotary evaporator, and the residual solid was chromatographed on neutral activity I alumina (elution with 10% chloroform in benzene) to furnish 1.0 g (67%) of **4c** as a white crystalline solid, mp 227.5–228.5° (from methylene chloride–hexane): ν_{max} ($CHCl_3$) 2900, 1769, 1700, and 1410 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.1–7.6 (br m, 5, aromatic), 4.6 (br t, J = 4 Hz, 2, >CH–N<), 3.5 (m, 2, methine), 2.84 (t, J = 3 Hz, 2, methine), and 1.2–2.1 (m, 10, methylenes).

Anal. Calcd for $C_{21}H_{21}N_3O_2$: C, 72.60; H, 6.09; N, 12.09. Found: C, 72.74; H, 6.08; N, 12.02.

Ag^+-Catalyzed Rearrangement of 4c. A solution containing 740 mg (2.13 mmol) of **4c,** 30 g (176 mmol) of silver nitrate, and 200 ml of isopropyl alcohol–water (4:1) was refluxed with magnetic stirring for 16 days in the absence of light, cooled, and diluted with methylene chloride. The organic phase was washed with water and brine, dried, and evaporated. Recrystallization of the residue from methylene chloride–hexane afforded 487 mg (66%) of **5c** as a white crystalline solid, mp 156–157°: ν_{max} ($CHCl_3$) 2900, 1750, 1700, 1400, 1130, and 909 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.23–7.68 (br m, 5, aromatic), 4.70–4.91 (m, 2, >CH–N<), and 1.10–2.17 (m, 13, cyclopropyl and methylenes).

Anal. Calcd for $C_{21}H_{21}N_3O_2$: C, 72.60; H, 6.09; N, 12.09. Found: C, 72.72; H, 6.08; N, 12.11.

2,8-Pentamethylenesemibullvalene [1a ⇄ 1b, X = $(CH_2)_5$]. A mixture of 281 mg (0.81 mmol) of **5c,** 719 mg (11.2 mmol) of potassium hydroxide (86.6%), and 15 ml of 2-propanol was heated at reflux for 1 hr under completely anaerobic conditions, cooled to 0°, and treated slowly with 3 *N* hydrochloric acid (deoxygenated) until a pH of 2 was reached. The acidic solution was stirred for 5 min, and the pH was adjusted to 8 with 3 *N* aqueous ammonia (deoxygenated). Pentane (10 ml) and methylene chloride (10 ml) were carefully introduced, followed by 802 mg (9.22 mmol) of active manganese dioxide. After this mixture had been stirred at room temperature for 4.5 hr, it was filtered through Celite, washed with water and brine, dried, and evaporated. Preparative vpc isolation (1 ft × 0.25 in. 5% SF-96 on Chromosorb G; column temperature 65°; detector temperature 95°, injector temperature 75°, flow rate = 350 cc/min) yielded 54.4 mg (39%) of the semibullvalene as a very light yellow oil: ν_{max} (neat) 3040, 2900, 1430, 1325, 1250, 935, 860, 800, 732, and 722 cm^{-1}; λ_{max} (isooctane) 238 sh nm (ϵ 3600); δ_{TMS} ($CDCl_3$) (35°) 4.98 (d, J = 2.7 Hz, 2, olefinic), 3.78–3.90 (m, 2, cyclopropyl-olefinic), 2.90–3.10 (m, 1, outer methine), 2.78 (d, J = 6 Hz, 1, inner methine), 2.38–2.65 (m, 4, allylic), and 1.40–2.10 (m, 6, methylene). Calcd: *m/e* 172.1252. Found: 172.1254.

[4.4.2]Propella-2,4,8,11-tetraene. To a magnetically stirred solution of 236 mg (1.49 mmol) of [4.4.2]propella-3,8,11-triene[11] in 20 ml of carbon tetrachloride–acetic acid (1:1) was added in one portion 506 mg (1.58 mmol) of pyridinium hydrobromide perbromide, and the solution was stirred at ambient temperature for 12 hr. The solution was diluted with ether, washed with water, 0.5 *N* sodium hydroxide solution, and brine, and dried. Removal of the solvent *in vacuo* (no heat) gave 469 mg (98.7%) of the 3,4-dibromide as a clear oil: ν_{max} (neat) 3000, 2890, 2810, 1250, 1220, 770, and 750 cm^{-1}; δ_{TMS} ($CDCl_3$) 5.7–6.4 (m, 4, olefinic), 4.5–5.1 (m, 2, CHBr), and 1.7–2.8 (m, 3, allyl and $-CH_2-CBr$).

To a magnetically stirred solution of 469 mg (1.47 mmol) of the dibromide in 20 ml of hexamethylphosphoramide were added 588 mg (14.0 mmol) of lithium chloride and 1.04 g (14.0 mmol) of lithium carbonate, and the slurry was heated at 85–90° for 22 hr under dry nitrogen, diluted with water, and extracted with pentane. The extract was washed with water (6×) and saturated salt solution and dried. The solution was passed through an alumina column, and the solvent was carefully removed through a metal helix-packed column [last traces removed at 20° (15 mm)] to give 152 mg (66.0%) of the tetraene **2d.** An analytical sample was obtained as a colorless oil by preparative vpc (10 ft × 0.25 in. 10% Carbowax 20M on Chromosorb W, 105°): ν_{max} (neat) 3010, 2880, 2790, 1070, 875, and 760 cm^{-1}; δ_{TMS} ($CDCl_3$) 5.42–5.97 (m with sharp s at δ 5.68, 8, olefinic) and 1.88–2.07 (m, 4, allyl); λ_{max} (isooctane) 268 (ϵ 2260), 230 (1960), and 223 nm (2320).

Anal. Calcd for $C_{12}H_{12}$: C, 96.26; H, 7.74. Found: C, 92.02; H, 7.85.

5,8-Dihydro-*N*-phenyl-1,4:4a,8a-diethenophthalazine-2,3(1*H*,4*H*)-dicarboximide (3d). To a magnetically stirred solution of 5.14 g (32.9 mmol) of [4.4.2]propella-2,4,8,11-tetraene in 125 ml of acetone at −78° was added dropwise 5.76 g (32.9 mmol) of *N*-phenyltriazolinedione in 125 ml of acetone. The solution was allowed to warm to room temperature, and after stirring for 0.5 hr the solvent was removed *in vacuo*. The yellowish crystalline residue was chromatographed on 500 g of alumina. Elution with chloroform–ether (1:3) gave 10.1 g of slightly yellow solid, recrystallization of which from benzene afforded 8.21 g (75.4%) of white crystalline **3d,** mp 253–255°. An analytical sample was obtained after recrystallization from ethyl acetate: ν_{max} ($CHCl_3$) 1760, 1720, 1690, 1490, and 1400 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.43 (m, 5, aromatic), 6.28, (t, J = 4.5 Hz, 2, olefinic), 5.78 (m, 4, cyclobutene and cyclohexene), 4.73 (br t, J = 4 Hz, 2, >CH–N<), and 2.2–2.7 (m, 4, allyl).

Anal. Calcd for $C_{20}H_{17}N_3O_2$: C, 72.49; H, 5.17; N, 12.68. Found: C, 72.07; H, 5.12; N, 12.41.

2,2a,6,9-Tetrahydro-*N*-phenyl-1,5a,2,5-ethanediylidene-5a*H*-cyclobuta[*d*]phthalazine-3,4(1*H*,5*H*)-dicarboximide (4d). A solution of 1.21 g (3.66 mmol) of **3d** in 450 ml of oxygen-free acetone was irradiated with a 200-W Hanovia lamp through a Vycor filter for 2 hr. The solvent was removed *in vacuo* to give a frothy yellow solid. Chromatography of this material was carried out on alumina (elution with chloroform–benzene (1:9)) to give 0.53 g (44%) of **4d** as a white crystalline solid, mp 184.0–186.0° (from acetone): ν_{max} ($CHCl_3$) 1760, 1700, 1500, and 1400 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.3–7.7 (br m, 5, aromatic), 5.82 (t, J = 2.5 Hz, 2, olefinic), 4.82 (t, J = 3.5 Hz, 2, >CH–N<), 3.64 (m, 2, methine), 2.91 (t, J = 3 Hz, 2, methine), and 2.38 (m, 4, allyl).

Anal. Calcd for $C_{20}H_{17}N_3O_2$: C, 72.49; H, 5.17; N, 12.68. Found: C, 72.39; H, 5.30; N, 12.68.

1a,2,3,6,7,7a-Hexahydro-*N*-phenyl-1,2a,6a-metheno-1*H*-cyclopropa[*b*]naphthalene-2,7-biimine-8,9-dicarboximide (5d). Into 200 ml of an anhydrous 0.2 *N* silver perchlorate benzene solution was added in one portion 859 mg (2.59 mmol) of **4d,** and the solution was stirred under reflux in the dark in a dry nitrogen atmosphere for 60 hr. The solvent was removed *in vacuo* and the residue was well triturated with hot chloroform, and the combined filtrates were washed with water (3×) and saturated salt solution and dried. Removal of the solvent *in vacuo* gave a clear oil which was chromatographed on alumina. Elution with 15% chloroform in ether gave 764 mg (89.0%) of **5d,** mp 148.0–150.0° (from ether):

ν_{max} ($CHCl_3$) 1770, 1700, 1500, 1400, 1290, and 1130 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.25–7.67 (br m, 5, aromatic), 5.50 (m, 2, olefinic), 4.9 (br t, J = 2.5 Hz, 2, >CH–N<), 2.52 (m, 4, allyl), and 1.90–2.12 (m, 4, cyclopropyl).

Anal. Calcd for $C_{20}H_{17}N_3O_2$: C, 72.49; H, 5.17; N, 12.68. Found: C, 72.26; H, 5.39; N, 12.46.

2a,5,7,8b-Tetrahydrobenzo[1,3]cyclopropa[1,2,3-*cd*]pentalene (1a ⇄ 1b, X = CH_2CH = $CHCH_2$). From 407 mg (1.23 mmol) of **5d** there was obtained in the manner employed for the tetramethylene example a dark yellow oil which afforded 70 mg (37%) of the semibullvalene as a clear oil after preparative vpc (4 ft × 0.25 in. 5% SF-96 on Chromosorb G, 80°): ν_{max} (neat) 3000, 2920, 2850, 2810, 1430, 1220, 1010, 840, 820, 750, and 730 cm^{-1}; δ_{TMS} ($CDCl_3$) 5.53, 5.57, and 5.61 (X portion of ABX system, $J \approx 1.5$ Hz, 2, cyclohexene), 5.04 (d, J = 4 Hz, 2, olefinic), 4.75 (t, $J \approx 4$ Hz, 2, pseudo-olefinic), 3.22 (pent, $J \approx 4$ Hz, 1, peripheral bridgehead proton), 2.92 (br s, 4, allyl), and 2.69 (d, J = 8 Hz, 1, interior bridgehead proton); λ_{max} (isooctane) 230–250 sh nm (ϵ 2000). Calcd: *m/e* 156.0938. Found: 156.0940.

Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.11; H, 7.62.

Also collected was a minor product (10 mg) with a longer vpc retention time than the semibullvalene. This material was shown by spectral comparison with an authentic sample to be benzocyclooctatetraene.[41]

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