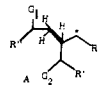

match still cannot be formed will an FGA subgoal be attempted at the starred carbon.

(20) The "appropriate distance" will, of course, depend on the nature of the particular goal transform toward which the subgoal sequence is leading. Since there is no a priori selection of *one* of the five or six candidate two-group transforms as a goal, several retrosynthetic pathways are generally developed which lead to several different ways to open a given strategic bond.

(21) Several different types of functional groups may be inserted since there are several different goal transforms which may be employed to cleave strategic bonds. Also, the atom to which the new group is attached will generally be one, two, or three atoms away from the strategic bond, depending on the type of group being inserted and, by extension, the nature of the goal transform being cleared by the subgoal. On the average, four or five antithetic routes are developed to break each strategic bond. Again, before any subgoal transform is applied to a molecule, it is subjected to a detailed evaluation step.[6]

(22) There is some analogy to the state of affairs in a contest in which knowledge of a strategy allows the foiling of that strategy.

(23) Nonetheless the strategic bond rules work well for the majority of structures based on **33**, and the cleavage of the starred bond in **33** guides the analysis toward an elegant and demonstrated synthetic plan; see J. E. McMurry, *J. Am. Chem. Soc.*, **90**, 6821 (1968).

(24) E. J. Corey, W. T. Wipke, R. D. Cramer, III, and W. J. Howe, *J. Am. Chem. Soc.*, **94**, 421 (1972).

(25) A search procedure guided by the strategy of chiral-center removal is currently being implemented in LHASA.

(26) "Given a plane graph *G*, *its geometric dual G** is constructed as follows: place a vertex in each region" (= chemical ring) "and, if two regions have an edge *x* in common, join the corresponding vertices by an edge *x** crossing only *x*." See F. Harary, "Graph Theory", Addison-Wesley, Reading, Mass., 1969, p 113.

(27) Arbitrarily all rings are depicted as six membered.

(28) N. Anand, J. S. Bindra, and S. Ranganathan, "Art in Organic Synthesis", Holden-Day, San Francisco, Calif., 1970.

(29) The perception of primary rings in LHASA is accomplished by means of a straightforward "spanning tree" algorithm. See K. Paton, *Commun. ACM*, **12**, 514 (1969).

(30) D. A. Pensak, Ph.D. Dissertation, Harvard University, 1972, p 76.

Probing of the Interrelationship between Heteroatomic Substitution and Equilibrium Imbalance in 2,8-Trimethylenesemibullvalene Derivatives[1]

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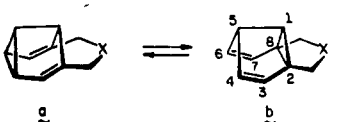
Abstract: To assess the magnitude and direction of equilibrium caused by certain electronegative atoms, three 2,8-annulated semibullvalenes have been synthesized. These molecules are directly patterned in structure after the 2,8-trimethylene bridged hydrocarbon which was known to exhibit approximately equal partiality for the two valence tautomeric forms at room temperature. For the three cases where the central methylene group was replaced in turn by O, S, and $NCH_2C_6H_5$, the equilibrium was shifted substantially in that direction where the cyclopropane ring occupies a central position in the molecule. The level of this imbalance was found to vary somewhat depending upon the particular hetero atom. The ^1H NMR spectra of the oxa- and thiasemibullvalenes show little temperature dependence in the range -120 to $+100°$. This feature suggests that entropy factors control the isomer distribution. Thus, although the hetero atoms are not bonded directly to the fluxional system, measurable ground state effects of significant magnitude are clearly in evidence.

Few, if any, organic molecules can be expected to attain the facility for Cope rearrangement which prevails in semibullvalenes.[4-6] This hydrocarbon ring system contains a *cis*-1,2-divinylcyclopropane moiety which is rigidly constrained into a folded conformation. The resulting cant of the internal cyclopropane σ orbital in relation to the two peripheral π bonds is such that electronic realignment in the [3.3]sigmatropic mode requires minimal activation energy.

Because valence isomerization in **1** is doubly degenerate,[7] there cannot exist a weighted thermodynamic preference

1a **1b**

for one of the two structures. Consequently, perturbational effects arising from framework substitution of semibullvalene should be directly assessable without added complication. This novel feature has commanded recent theoretical[8,9] and experimental attention.[10-12] For monosubstituted semibullvalenes, variable temperature ^1H NMR studies have denoted preferential bonding to olefinic > cyclopropyl > aliphatic carbon, irrespective of the location and nature of the R group.[10,11] The response to bracketing effects is recognized to be more delicate.[5,12] For example, 2,8-bridging with a trimethylene chain to give **2** seemingly stabilizes the pair of tautomers almost equally, **2b** being favored to the extent of only 57% at $+40°$. Equal distribution of the two isomers exists at $-29°$ (CS_2 solution) and **2a** dominates the equilibrium below this temperature. For the tetramethylene case (**3**), only limited spectral changes are noted throughout a wide temperature range. Valence tautomer **3a** is substantially favored under these conditions. As concerns **4**, a preference for **4a** (58%) exists at $+40°$ (CS_2 solution); in the vicinity of $+17°$, however, crossover occurs and **4b** is favored at the lower temperatures. The responses of **2** and **4** to changing temperature are therefore diametrically opposite. The causative factors are of course due to the varying importance of the $\Delta H°$ and $T\Delta S°$ terms to the individual equilibria.[12]



2a **2b**

2, X = CH_2
3, X = CH_2CH_2
4, X = $(CH_2)_3$

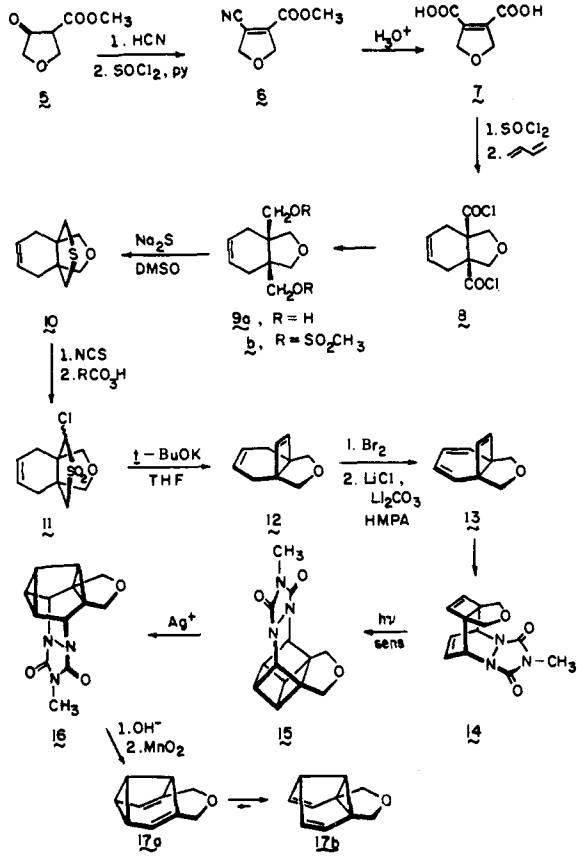
Because the semibullvalene nucleus serves particularly well as a fine-tuning device for the probing of ground state perturbational effects, a detailed systematic investigation of

substituent influences is warranted. We have now constructed a trio of molecules patterned after **2** in which the methylene group most remote from the semibullvalene ring (i.e., X) has been replaced by O, S, and $NCH_2C_6H_5$. Although the size and electronegativity demand of the heteroatoms do, of course, vary, their relative position remains constant. As will be seen, the equilibrium imbalances arising from such varied annulation are directly correlatable to a combination of differential strengthening influences exerted upon the central cyclopropane bond and a general diminution in eclipsing interaction.

Synthetic Considerations

Modification of Hetero Propellanes. The desired oxa derivative **17** was synthesized via the route depicted in Scheme I. The sequence is patterned after the successful

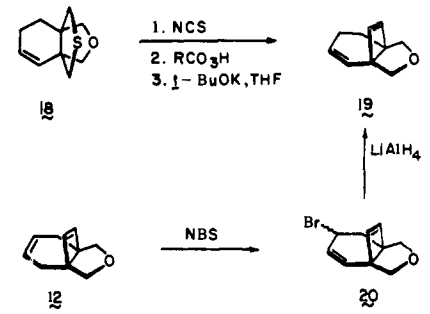
Scheme I



preparation of **2**[12] and is dependent upon the availability of oxapropellatriene **13**. Two observations made while gaining access to **13** are noteworthy. Firstly, because 2,5-dihydrofuran-3,4-dicarboxylic anhydride gave evidence of instability, the Diels–Alder condensation was effected instead with the equally reactive bis(chloroformyl) derivative. High yields (~95%) of adduct **8** were consistently realized. Secondly, the cyclization of **9b** to sulfide **10** was accompanied by formation of double bond isomer **18** in varying amounts (0–34%). This compound, found to be inseparable from **10** by the usual methods, is the obvious result of a prototropic shift under rather mild conditions. Its structure was established by Ramberg–Bäcklund rearrangement[13] to **19**, an alternate, unequivocal synthesis of which was devised starting with **12** (Scheme II). That allylic bromination of **12** should proceed with 1,2 migration of the double bond is precedented in such tricyclic systems.[14]

The instantaneous cycloaddition of *N*-methyltriazolinedione to **13** in cold (−70°) acetone solution afforded **14**

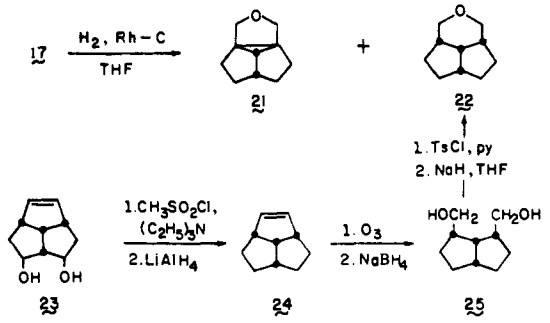
Scheme II



in 93% yield. The *N*-methyl derivative was utilized because compounds **14–16** are more soluble than their *N*-phenyl counterparts, and the by-product from the hydrolysis-oxidation procedure (i.e., **16** → **17**) is volatile methylamine rather than aniline. That ($_{\pi}4 + _{\pi}2$) bonding to **13** proceeded cleanly from that direction proximate to the hetero ring was established by acetone-sensitized photocyclization of **14** to **15**. Attempted silver(I) catalyzed rearrangement of **15** with the silver perchlorate–anhydrous benzene and silver nitrate–aqueous isopropyl alcohol systems[15] led to recovered starting material. However, dissolution in dioxane–water (4:1) containing silver nitrate and heating at 130° (sealed tube) for 4 days provided **16** in 65% yield. When hydrolyzed and oxidized under argon, **16** was transformed via the labile diazasnoutene[10] to the low-melting crystalline ether **17**.

Confirmation of the gross structural features of this semibullvalene was achieved by catalytic hydrogenation in anhydrous tetrahydrofuran over 5% rhodium on carbon. Somewhat more than 2 mol equiv of hydrogen was consumed to give saturated ethers **21** and **22** in a 1:1 ratio (Scheme III). One of these (**21**) proved to be $C_{10}H_{14}O$ in

Scheme III

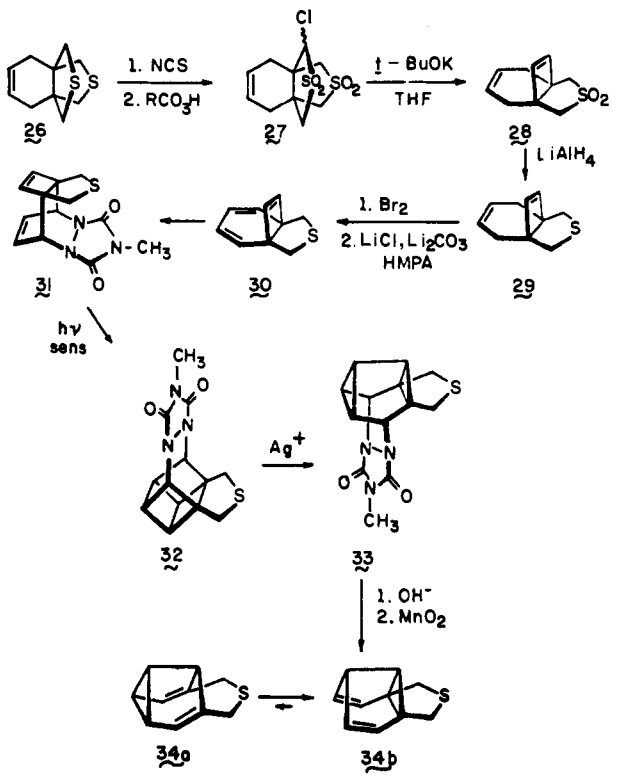


nature, while the second component contained two additional hydrogens. This white crystalline solid was identified by direct comparison with an authentic sample prepared as outlined from tetrahydrotriquinacene (**24**). The intrinsic stereochemistry was thereby also established.

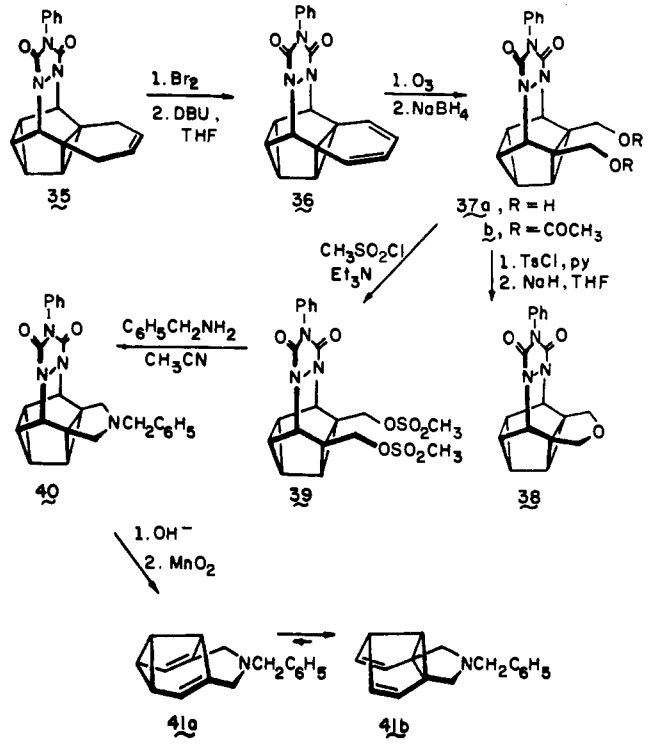
The successful synthesis of thiasemibullvalene **34** is summarized in Scheme IV. The known sulfide **26**, upon sequential α-chlorination with 1 equiv of *N*-chlorosuccinimide, oxidation with 4 equiv of monoperphthalic acid,[16] and exposure to potassium *tert*-butoxide, was transformed to sulfone **28** in 42% overall yield. Although bromination–bisdehydrobromination of **28** led to resinification, this problem was circumvented by initial reduction to **29**. The subsequent conversion to triene sulfide **30** proceeded smoothly. Bond reorganization in **32** under the influence of silver catalysis could again be effected successfully (62% yield) in dioxane–water (4:1) at 130° for 4 days. Structural assignment to semibullvalene **34** follows convincingly from its mass and ^1H and ^{13}C NMR spectral features (vide infra).

Functionalization of a Common Diazasnoutane. Although Schemes I and IV serve to provide quite adequate quantities

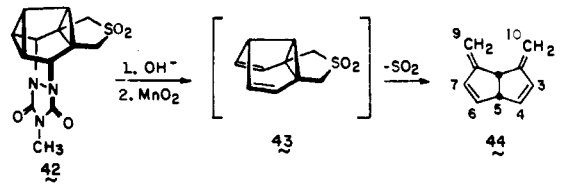
Scheme IV



Scheme V



Scheme VI



of **17** and **34**, these synthetic approaches run parallel and are necessarily duplicative rather than complementary. The latter goal could be achieved, however, if the heteroatom were introducible at some point late in the sequence. Such a development would provide a more ready and direct route to these (and other) functionalized semibullvalenes.

In principle, it seemed likely that diol **37a** might fulfill the necessary requirements provided that the solvolytic reactivity of its derivatives was not excessively high. This question was addressed by bromination–bisdehydrobromination of the known diazasnoutane **35**[12] to give diene **36**. Subsequent ozonolysis and sodium borohydride reduction of **36** proceeded smoothly with formation of the desired diol, characterization of which as diacetate **37b** proved convenient (Scheme V). Ready cyclization to **38** was achieved by conversion of **37a** to its monotosylate, followed by treatment with sodium hydride according to the method of Wolff, Smith, and Agosta.[17] The numerous spectral similarities between **38** and its *N*-methyl counterpart (**16**) comprise the basis for structural assignment. Whereas the formation of **38** indicates that the monotosylate can survive reasonable synthetic manipulation without rearrangement, the somewhat analogous preparation of pyrrolidine **40** establishes the corresponding dimesylate (**39**) likewise to be a serviceable intermediate. Qualitative comparison of the oxa- and thiasemibullvalenes with amine **41** revealed the latter to be the most labile of the three derivatives and to undergo polymerization with relative ease at ambient temperature.

Attempted Formation of the Sulfone Derivative. In efforts directed toward the preparation of sulfone **43**, parent sulfide **34** was treated with 2 equiv of purified *m*-chloroperbenzoic acid in chloroform. Total decomposition with dark coloration of the solution occurred immediately. Such findings discouraged further efforts along these lines. Attention was next turned to oxidation of diazasnoutane **33**. No difficulties were encountered and **42** was isolated in 82% yield (Scheme VI). The infrared bands and ^{1}H NMR patterns of **42** are fully consistent with the assigned structure (see Experimental Section). When subjected to hydrolysis and oxidation under carefully controlled conditions, **42** did not furnish **43** but the $C_{10}H_{10}$ hydrocarbon **44** instead. Structure **44** was adduced from its ultraviolet spectrum [$\lambda_{max(isooctane)}$ 219 nm (ϵ 26,000) and 250 sh (6400)] and from NMR data. The emergent ^{1}H NMR signals ($CDCl_3$ solution) provide clear evidence for four ring olefinic protons (δ 6.02, br s), two pairs of exomethylene hydrogens [5.02 (d, J = 1.4 Hz), 4.96 (d, J = 1.8 Hz)], and two different doubly allylic protons [4.02 (d, J = 6 Hz), 3.82 (m)]. The inherent symmetry of this tetraene was further revealed by its ^{13}C NMR spectrum which features six signals at 156.6, 139.5, 133.0, 105.0, 58.5, and 48.6 ppm downfield from Me_4Si. Both data confirm the C_s symmetry of the molecule and rule out the possibility that the methylene groups are positioned in a C_2,C_5 relationship (C_2 symmetry).

Since sulfone **42** can be recovered unchanged after being heated at 80° in CD_3CN for 2 hr (sealed NMR tube), **44** presumably arises by cheletropic extrusion of sulfur dioxide in **43**. That this elimination proceeds with unprecedented facility[18] was demonstrated when the manganese dioxide oxidation of hydrolyzed **42** and attendant work-up were accomplished at temperatures not exceeding 25°.

NMR Results

Proton Magnetic Resonance Data. It will be recalled that the 100-MHz ^{1}H NMR spectrum of 2,8-trimethylenesemibullvalene (**2**) at +40° ($CDCl_3$ solution, see Figure 1) is characterized by a 2:2:2:4:2 ratio of peaks,[12] the relevant chemical shifts of which correspond closely to those of semibullvalene.[6,7] Judging from the values of δ_v (5.59) and δ_c (2.34) experimentally determined for nonfluxional 2,8-pen-

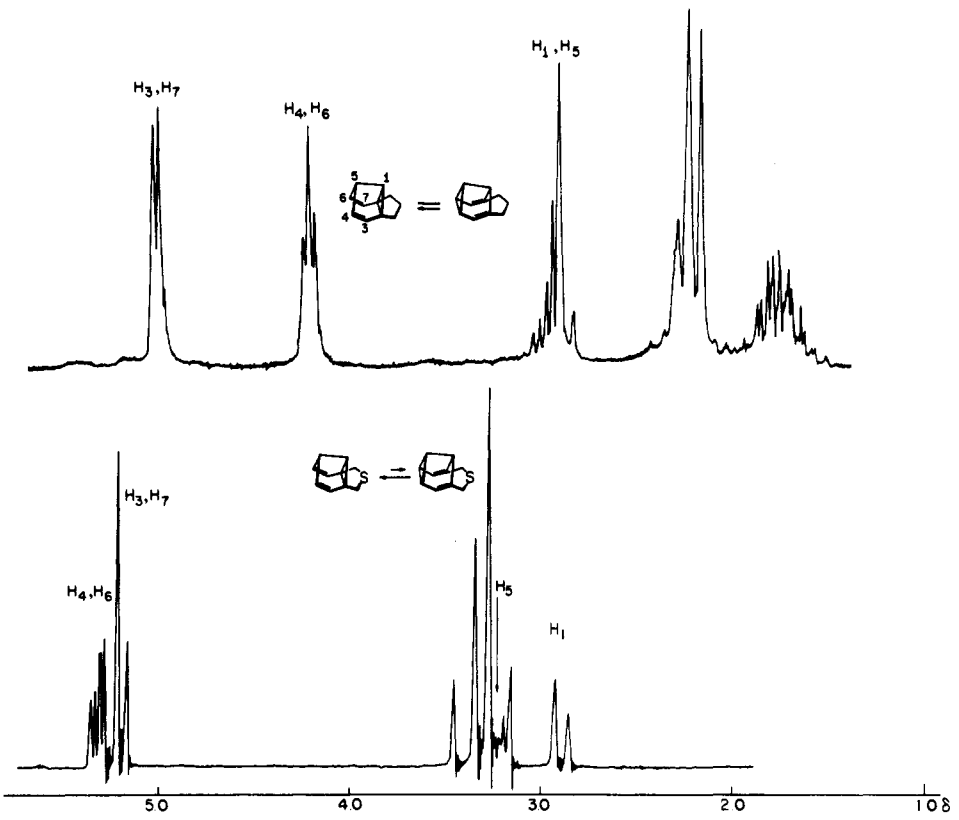


Figure 1. ^{1}H NMR spectra (100 MHz) of: (top) 2,8-trimethylenesemibullvalene (**2**) in $CDCl_3$ at +40°; (bottom) thiasemibullvalene (**34**) in CS_2 at +40° (500 Hz sweep width).

tamethylenesemibullvalene (**4**) at −120°,[5] an equilibrium constant of 0.75 favoring **2b** was calculated. Variable temperature studies in the range of +45 to −91° (CS_2 and C_2Cl_4 solutions) revealed a crossover in the direction of equilibrium below −29° with $\Delta H°$ equal to −315 cal/mol and $\Delta S°$ being slightly negative (−1.3 eu).

Replacement of the central carbon atom of the trimethylene bracket with an oxygen atom produces a marked shift in the equilibrium. This is demonstrated in the room temperature spectrum (in CS_2) where the chemical shift of the time-averaged protons H_4,H_6 (δ 5.58) indicates the presence of nearly 100% of tautomer **17b**. Due to the symmetry of this molecule and the wide chemical shift differences of each set of protons, the spectrum of **17** is first order, thus allowing for ready analysis of coupling constants (see Experimental Section). Variable temperature ^{1}H NMR analysis from −100 (CS_2) to +70° (C_2Cl_4) did not reveal measurable alteration of the isomer distribution.

Like **17**, thiasemibullvalene **34** was found to experience weighting in the **34b** direction (Figure 1). However, the effect is somewhat less dramatic, the isomer with the central cyclopropane ring now dominating by a level of approximately 90%. This is seen to be an isomer ratio opposite to that experienced by tetramethylene derivative **3**. Unlike **3**, the thia compound exhibited weak temperature dependence with isomer **34b** increasing in relative concentration as the temperature is lowered (to −120°, CS_2) and decreasing with incremental temperature increases (to +100°, C_2Cl_4, Table I). By plotting ln K_{eq} vs. $1/T$ (CS_2 data only), the thermodynamic parameters $\Delta H° \approx 0$ and $\Delta S° = -8.8$ eu were obtained.

The H_4,H_6 protons in aza derivative **41** give rise to a time-averaged signal centered at δ 5.36 (Figure 2). On the basis of this chemical shift, the approximate isomer distribution in **41** is seen to be intermediate between that of the oxa and thia compounds (Table II). Application of the standard equation[12,19] to this datum showed **41b** to be present above the 92.9% level at 40°. The resonances of the various sets of protons are again nicely resolved even at 60 MHz, the signal for the permanently olefinic protons being found on the upfield side of the population revealing doublet of doublets due to H_4,H_6. Alterations in the ground state distribution of the **a** and **b** forms with changing temperature were expected to be small and were not examined.

Table I. Variable Temperature ^{1}H NMR Data (100 MHz, CS_2 for Room Temperature and below, C_2Cl_4 for above Room Temperature), Computed Equilibrium Constants (K_{eq}), and Gibbs Free Energy Values ($\Delta G°$) for the Fluxional System 34a ⇄ 34b

Temp, °C	Chemical shift H_4, H_6, δ	Mol fraction 34b × 10^2	K_{eq} (34a/34b)	Ln K_{eq}	$\Delta G°$, cal/mol
100	5.26	89.8	0.114	−2.18	1620
80	5.29	90.8	0.101	−2.29	1610
68.5	5.30	91.1	0.0977	−2.33	1580
51	5.32	91.7	0.0905	−2.40	1550
32.5	5.33	92.0	0.0870	−2.44	1480
−19	5.38	93.5	0.0695	−2.67	1350
−43	5.41	94.5	0.0582	−2.84	1300
−69	5.44	95.4	0.0482	−3.03	1230
−78	5.45	95.7	0.0449	−3.10	1200
−110	5.48	96.6	0.0352	−3.35	1090
−120	5.49	96.9	0.0320	−3.44	1050

Carbon-13 Chemical Shifts. The valence isomeric equilibrium of semibullvalene has previously been investigated by ^{13}C NMR spectroscopy.[6,20] The properties of the parent hydrocarbon with its rapidly equilibrating pair of degenerate isomers are such that only three widely spaced signals at 50.0, 86.5, and 120.4 ppm appear at ambient temperature, assignable to $C_{1,5}$, $C_{2,4,6,8}$, and $C_{3,7}$, respectively.[20] Large displacements of the equilibrium position such as encountered with the present hetero trimethylenesemibullvalenes, while not affecting greatly the rate of Cope rearrangement

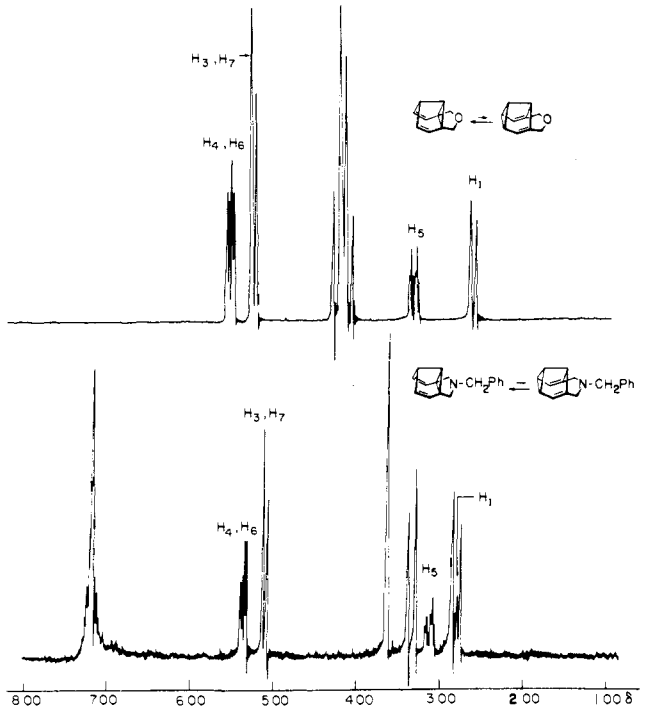


Figure 2. ^{1}H NMR spectra (100 MHz) in CS_2 solution of oxasemibullvalene **17** and *N*-benzylazasemibullvalene (**41**) at +40° (1000 Hz sweep width).

Table II. ^{1}H NMR Data (60 MHz, $CDCl_3$), Computed Equilibrium Constants (K_{eq}), and Gibbs Free Energy Values (ΔG°) for **2**, **17**, **34**, and **41** (40°)

Bracket substituent	Chemical shift, H_4, H_6, δ	Mol fraction isomer b (10^2)[a]	K_{eq}, a/b	ΔG°, cal/mol
CH_2	4.21	57	0.75	175
O	5.58	99.7	3×10^{-3}	3600
S	5.25	89.5	0.12	1320
$NCH_2C_6H_5$	5.36	92.9	7.6×10^{-2}	1600

[a] The method employed is not considered to provide accuracy levels of better than 1% at best. The values cited are computational in origin, and appropriate error limits should be recognized by the reader.

(and consequently the rapid time averaging of the carbon atoms), do generate significant perturbations of the chemical shift values. The relevant data which are summarized in Table III clearly show the central carbon atoms ($C_{2,8}$) to be much more cyclopropanoid and the peripheral carbons ($C_{4,6}$) to be substantially more olefinic than the respective centers in semibullvalene. The trend O > NCH_2Ph > S parallels that observed by ^{1}H NMR and supports the earlier conclusions relating to the several tautomer distributions. It is important to recognize that carbons 2 and 8 are positioned β to the individual heteroatoms and consequently can be expected to exhibit more varied shifting because of usual substituent effects. Since C_4 and C_6 are positioned on the opposite side of the molecular frame, however, they should be reasonably well insulated from such factors.

Discussion

The identification of **45a** as the dominant valence tautomer resulting from methyl substitution of semibullvalene at $C_{2,4}$[10] substantiates the conclusion drawn earlier from theoretical findings[8,9] that an electron-releasing group[21] exerts an electronic effect within the molecule which alters

Table III. Summary of ^{13}C NMR Data (22.6 MHz, $CDCl_3$, Ambient Temperature)

Semibullvalene	Chemical shifts, ppm from Me_4Si					
	C_1	$C_{2,8}$	$C_{3,7}$	$C_{4,6}$	C_5	α[a]
17	53.6[b]	61.7	121.0	127.6	52.8[b]	63.4
34	53.1[b]	73.2	119.3[c]	123.3[c]	52.9[b]	31.7
41[d]	53.8[b]	61.5	121.9	125.4	52.7[b]	53.9[b]

[a] Relates to the carbon atoms of the bracket with the α position being most proximal to the semibullvalene nucleus. [b] These values may be interchanged. [c] These values may be interchanged. [d] 59.4: benzyl; 126.9, 128.1, 128.7, and 139.0: aryl carbons.

the relative potential energies in such a way as to favor bonding to olefinic carbon (by ca. 1 kcal/mol at 40° for **45a**). Direct extrapolation of this type of analysis to 2,8-di-

45a **45b**

alkylated semibullvalenes would predict still greater partiality for tautomer **a**, barring possible steric contributions. In this context, the behavior of 2,8-tetramethylene derivative **3** forms a consistent pattern since the molecule exists chiefly (90%) as **3a** at 40° (ΔG° = 1.36 kcal/mol).[12] The ^{1}H NMR spectra of **3** are weakly temperature dependent and therefore ΔH° for this system seemingly approaches zero with entropy control prevailing throughout the entire temperature range. The translational contributions to **3a** and **3b** are likely to be very similar because the moments of inertia are quite comparable. Vibrational contributions, on the other hand, could be different, and an entropy imbalance of 1-2 eu is explainable in these terms. We emphasize, however, that the determination of ΔH° and ΔS° from small changes in chemical shifts over a very large temperature range is fraught with difficulties when the equilibrium is one sided as occurs for **3** and the three compounds in Table II. A not easily discounted possibility is that the entropies are in error due to the temperature dependence of the chemical shifts of the two tautomers.

Previously, we also synthesized 2(4)-methoxymethylsemibullvalene (**46**) and observed the predominant species in solution (+30°) to be that in which the substituent was bonded to olefinic carbon.[10] A similar persistence for attachment to a trigonal center upon introduction of a β oxygen atom ($-CH_2OH$ as well as $-CH_2OCH_3$)[10] does not carry over to the annulated analog. In the present work, the equilibrium associated with oxasemibullvalene **17** is seen to be displaced heavily in the **b** direction where preferred bonding to the cyclopropane ring is made possible.

This intriguingly divergent behavior, which at first glance may appear totally anomalous, likely has its origins in the special features found in annulated semibullvalenes. The response of the semibullvalene frame to methoxymethyl (acyclic) substitution agrees in principle with adjacent bond weakening effects and is understandable on the basis of enthalpy control. For **17** on the other hand, ΔH° may approach zero (compare thermodynamic parameters for the thia derivative), and ΔG° will consequently be roughly proportional to $-T\Delta S^\circ$. Isomer **17b** is expected a priori to enjoy still greater degrees of freedom than trimethylene congener **2b** because of substantial diminution in the level of nonbonded eclipsing interactions by vicinal hydrogens. Accordingly, **17b** should be favored to a greater extent than **2b** on this basis, and it is.

The greater level of conformational freedom available to **17b** should also be shared by **34b** and **41b**, and this is evidently so. However, we note a trend in which tautomer **a**

gains added weighting as progression is made through the series O < $NCH_2C_6H_5$ < S (Table II). The compilation of physical data found in Table IV serves to group various recognized phenomena associated with these three atoms. All such data are reconcilable with the notion that structural enlargement of the bracket and lessening of electronegativity demands by group X work together to approach the nature of tetramethylene bridged system **3** where valence isomer **a** is now intrinsically favored.

In summary, we emphasize that 2,8-annulated semibullvalenes can reveal, by means of spectroscopically detectable equilibrium imbalances, the existence of subtle libration effects not visible by other techniques. The varied ground state behavior of such molecules can be expected to provide meaningful data relating to ring constraint phenomena and entropic differences between pairs of valence isomeric structures. With these goals in mind, studies in this direction are continuing.

Experimental Section

Proton magnetic resonance spectra were recorded with Varian A-60A, Varian HA-100, and Jeolco MH-100 instruments, while carbon magnetic resonance spectra were obtained with a Bruker 90 spectrometer. Apparent splittings are given in all cases. Infrared spectra were recorded on Perkin-Elmer Model 137 and 467 spectrometers, whereas mass spectra were obtained with a CEI-MS9 instrument at an ionizing potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

3-Carbomethoxy-4-cyano-2,5-dihydrofuran (6). To a stirred solution of sodium cyanide (112 g, 2.3 mol) in 100 ml of water was added 110 g (0.76 mol) of **5**[22] in 1 l. of ether. After this mixture had been cooled in an ice bath, 132 ml of 18 *N* sulfuric acid was added over a period of 1.5 hr. After stirring the room temperature solution overnight, the excess hydrogen cyanide was removed under reduced pressure, and the organic solution was decanted from the salts which were washed twice with benzene. After drying and evaporation of solvent, the crude cyanohydrin (ν_{max}(neat) 3400 and 1730 cm^{-1}) was dissolved in 182 g of cold pyridine and treated with 274 g (2.3 mol) of thionyl chloride during 1.5 hr at 0° under nitrogen. The resulting red solution was warmed to room temperature, stirred for 6 hr, slowly poured into 1.5 l. of ice and water, and extracted with benzene. The combined extracts were dried and concentrated in vacuo to afford, after short path distillation [80° (0.6 mm)], 96 g (82%) of light yellow solid. Further purification by recrystallization (ether) afforded white crystals: mp 71–72°; δ_{Me_4Si} ($CDCl_3$) 4.9 (s, 4, $-CH_2O-$) and 3.86 (s, 3, $-OCH_3$).

Anal. Calcd for $C_7H_7NO_3$: C, 54.90; H, 4.61. Found: C, 55.21; H, 4.74.

2,5-Dihydrofuran-3,4-dicarboxylic Acid (7). A solution of unpurified **6** (83.5 g, 0.546 mol) in 500 ml of concentrated hydrochloric acid was heated to reflux to yield a tan solid. Continued heating gave a brown solution which was diluted with 300 ml of water and refluxed for an additional hour. Filtration of the ice-cold mixture afforded 67.4 g (78%) of **7**, mp 179–186°.

In a similar manner, 15.3 g (0.1 mol) of recrystallized **6** was converted to 13.1 g (83%) of **7**, mp 191–193°. Recrystallization from ethyl acetate afforded white crystals, mp 191–193°.

Anal. Calcd for $C_6H_6O_5$: C, 45.58; H, 3.83. Found: C, 45.54; H, 3.90.

***cis*-1,6-Bis(chloroformyl)-8-oxabicyclo[4.3.0]non-3-ene (8).** A mixture of **7** (2.0 g, 12.6 mmol) in 10 ml of thionyl chloride was slowly warmed to reflux. After the diacid had dissolved, reflux was continued for an additional 2 hr. The usual work-up afforded 1.8 g (74%) of diacid chloride as a yellow liquid, bp 80° (0.3 mm); ν_{max} (neat) 1770 cm^{-1} (br); δ_{Me_4Si} ($CDCl_3$) 5.8 (s). The ^1H NMR spectrum also showed the presence of anhydride (11%).

A mixture of diacid chloride (1.8 g, 9.23 mmol), 10 ml of benzene, a few crystals of hydroquinone, and 10 ml of butadiene was heated in a heavy wall sealed glass vessel at 105° for 12 hr. The cooled reaction mixture afforded, after distillation, 2.2 g (95%) of **8**, bp 120° (0.3 mm), as a liquid which solidified upon standing:

Table IV. Selected Atomic Parameters[a]

Atom	van der Waals radii, A	Covalent single bond radii	Average C–X bond lengths, A[b]	Electronegativity
O	1.40	0.66	1.43	3.5
N	1.5	0.70	1.47	3.0
S	1.85	1.04	1.82	2.5

[a] Data taken from L. Pauling "Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, unless otherwise noted. [b] See also "Tables of Interatomic Distances and Configuration in Molecules and Ions", *Chem. Soc. Spec. Publ.*, No. 11 (1958).

ν_{max} (neat) 1780 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.7 (s, 2, olefinic), 4.16 (ABq, J_{AB} = 9 Hz, $\Delta\nu_{AB}$ = 50.2 Hz, 4, $-CH_2O-$), and 2.64 (m, 2, allylic). The ^1H NMR spectrum also contained absorptions due to the anhydride adduct.

***cis*-1,6-Bis(hydroxymethyl)-8-oxabicyclo[4.3.0]non-3-ene (9a).** To a refluxing slurry of lithium aluminum hydride (0.57 g, 15 mmol) in 20 ml of anhydrous tetrahydrofuran was added dropwise under nitrogen 2.2 g (8.87 mmol) of crude **8** in 15 ml of the same solvent, and the mixture was refluxed for 2.5 hr. After quenching the stirred, ice-cold slurry with a saturated sodium sulfate solution, the white salts were removed by filtration and leached with hot tetrahydrofuran. The combined filtrates were dried and evaporated to afford 1.5 g (92%) of **9a** as a yellowish solid, mp 181.5–185°. Further purification by recrystallization (chloroform–ether–hexane) afforded white needles: mp 193–195°; ν_{max} (KBr) 3340 (br), 3035, and 2890 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.66 (m, 2, olefinic), 4.6 (br s, 2, –OH), 3.72 (ABq, J_{AB} = 9 Hz, $\Delta\nu_{AB}$ = 18.3 Hz, 4, $-CH_2O-$), 3.64 (br s, 4, $-CH_2OH$), and 1.9–2.36 (br m, 4, allylic).

***cis*-1,6-Bis(methanesulfonyloxymethyl)-8-oxabicyclo[4.3.0]non-3-ene (9b).** A mechanically stirred cold (−10°) solution of methanesulfonyl chloride (195 g, 1.7 mol) in 1.5 l. of pyridine was treated dropwise with a solution of 103.2 g (0.562 mol) of recrystallized **9a** in 1 l. of the same solvent under a nitrogen blanket. After being stirred at −5° for 3 hr, the mixture was quenched with sufficient ice to destroy the excess sulfonyl chloride and diluted to ca. 7 l. with cold 10% hydrochloric acid (pH 1). The solution was allowed to stand at 0° for 1–2 hr, whereupon the precipitate was filtered, washed with cold water, and dried in vacuo (0.02 mm) at room temperature for 24 hr. There was obtained 183.7 g (96%) of **9b**, mp 103–104.5°. Further purification by recrystallization (chloroform–ether) afforded white crystals, mp 106.5–107°; ν_{max} (KBr) 1345, 1170, 945, 843, and 830 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.74 (br t, J = 1.5 Hz, 2, olefinic), 4.25 (s, 4, $-CH_2OSO_2Me$), 3.85 (ABq, J_{AB} = 8.8 Hz, $\Delta\nu_{AB}$ = 11.7 Hz, 4, $-CH_2O-$), 3.06 (s, 6, $-OSO_2CH_3$), and 2.26 (br s, 4, allylic).

Anal. Calcd for $C_{12}H_{20}O_7S_2$: C, 42.34; H, 5.92; S, 18.84. Found: C, 42.23; H, 5.90; S, 18.82.

8-Oxa-11-thia[4.3.3]propell-3-ene (10). A mixture of recrystallized (ethanol) sodium sulfide nonahydrate in 3 l. of dimethyl sulfoxide was dehydrated by means of vacuum distillation [maximum distillate temperature 85° (30 mm)]. To this cooled yellow mixture was added 291 g (0.856 mol) of recrystallized **9b** in one portion, and the mixture was heated under nitrogen to 120° for 18 hr. The mixture was again cooled (0°), diluted to a volume of 4 l. with cold water, and extracted with ether (7 × 500 ml). The combined ethereal extracts were washed with brine, dried, and concentrated in vacuo to afford a clear liquid which, after column chromatography on neutral activity I alumina (ether elution), amounted to 133 g (85%) of solid, mp 82–85°. A small portion of this solid was sublimed at 100° (25 mm) to afford **10** as a white solid: mp 93.5–95.5°; ν_{max} ($CHCl_3$) 2920, 2860, 1430, and 1035 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.72 (br t, J = 2 Hz, 2, olefinic), 3.76 (ABq, J_{AB} = 9 Hz, $\Delta\nu_{AB}$ = 9.2 Hz, 4, $-CH_2O-$), 2.86 (ABq, J_{AB} = 12 Hz, $\Delta\nu_{AB}$ = 7.1 Hz, 4, $-CH_2S-$), and 2.22 (m, 4, allylic); *m/e* (calcd 182.0765) 182.0768.

Oxidation of a small sample of the sublimed sulfide with 2 equiv of a standardized monoperphthalic acid solution afforded the more crystalline sulfone, mp 154.5–155.5° (chloroform–hexane); ν_{max} (KBr) 2860, 1320, 1300, 1230, 1174, 1123, 938, 711, 705, and 485 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.86 (m, 2, olefinic), 3.79 (ABq, J_{AB} = 9 Hz, $\Delta\nu_{AB}$ = 22.8 Hz, 4, $-CH_2O-$), 3.13 (ABq, J_{AB} = 13.3 Hz,

$\Delta\nu_{AB}$ = 15.4 Hz, 4, $-CH_2SO_2-$), and 2.10–2.60 (series of multiplets, 4, allylic).

Anal. Calcd for $C_{10}H_{14}O_3S$: C, 56.05; H, 6.59; S, 14.96. Found: C, 55.90; H, 6.47; S, 14.85.

7-Chloro-11-oxa-8-thia[4.3.3]propell-3-ene 8,8-Dioxide (11). To a solution of 27.3 g (150 mmol) of **10** in 225 ml of ice-cold carbon tetrachloride was added 21.0 g (157.5 mmol) of recrystallized *N*-chlorosuccinimide in one portion under nitrogen. After stirring at 0° for an additional 30 min, the solution was allowed to warm to room temperature for 2 hr. Removal of the succinimide and evaporation of the solvent afforded a waxy residue which was dissolved in 1 l. of anhydrous ether. To this ice-cold ethereal solution was added dropwise a standardized ethereal solution containing 0.315 mol of monoperphthalic acid under nitrogen. After this solution had been stirred at room temperature overnight, the precipitated phthalic acid was removed by filtration, and the filtrate was washed with 0.5 *N* sodium hydroxide solution and brine and dried. Solvent removal in vacuo afforded 35 g (94%) of **11** as a viscous oil: ν_{max} ($CHCl_3$) 1330, 1150, 1130, and 1060 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.89 (m, 2, olefinic), 4.92 and 4.70 (s, 1, >CHCl, ratio 1:2), 3.08–4.33 (continuous series of multiplets, 7, $-CH_2O-$ and $-CH_2SO_2-$), and 2.3 (br s, 4, allylic); *m/e* (calcd 248.0274) 248.0277.

8-Oxa[4.3.2]propella-3,10-diene (12). To an ice-cold mechanically stirred solution of **11** (35 g, 141 mmol) in 2 l. of anhydrous tetrahydrofuran was added 63.0 g (0.564 mol) of commercial powdered potassium *tert*-butoxide in one portion under nitrogen. After stirring for 30 min at 0°, the solution was refluxed for 4 hr. The cooled dark solution was diluted with 2 l. of cold water and extracted with pentane (8 × 200 ml). The combined extracts were washed with brine, dried, and concentrated in vacuo to afford a viscous oil which, after vacuum distillation, afforded 8.1 g (39%) of **12** as a clear liquid, bp 72° (5 mm). Preparative GLC on 5% Carbowax 20M (3 ft) at 85° afforded pure **12:** ν_{max} (neat) 3030, 2910, 2830, 1080, 1035, and 779 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.94 (s, 2, cyclobutenyl), 5.80 (dd, J = 3, 2.5 Hz, 2, olefinic), 3.47 (ABq, J_{AB} = 9.3 Hz, $\Delta\nu_{AB}$ = 42.2 Hz, 4, $-CH_2O-$), and 2.12 (m, 4, allylic).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.65; H, 8.49.

There was also obtained isomer **19** in 14% yield: ν_{max} (neat) 3025, 2920, 2835, 1040, 928, 873, and 780 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.99 (ABq, J_{AB} = 2.5 Hz, $\Delta\nu_{AB}$ = 18.6 Hz, 2, cyclobutenyl), 5.6–6.08 (br m, 2, olefinic), 3.88 (dd, J = 9.5, 5 Hz, 2, $-CH_2O-$), 3.06 (d, J = 9.5 Hz, 2, $-CH_2O-$), 1.7–2.2 (br m, 3, methylene), 1.1–1.45 (m, 1, methylene); *m/e* (calcd 148.0888) 148.0891.

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.01; H, 8.39.

8-Oxa[4.3.2]propella-2,4,10-triene (13). To a solution of distilled **12** (2.2 g, 14.8 mmol) in cold (−70°) methylene chloride was slowly added under nitrogen 15.1 mmol of bromine in methylene chloride. After warming to room temperature, the solvent was removed in vacuo to give 4.8 of yellow semisolid which was used without further purification.

A solution of this dibromide in 100 ml of anhydrous hexamethylphosphoramide was treated with 6.3 g (0.148 mol) of lithium chloride and 11.0 g (0.148 mol) of lithium carbonate, and the stirred slurry was heated at 90° for 16 hr under nitrogen. After cooling, the slurry was diluted with water and extracted several times with pentane. The combined extracts were washed with brine, dried, and passed through a neutral activity I alumina column to afford after vacuum distillation 1.46 g (67%) of **13** as a clear oil. Preparative GLC on 5% Carbowax 20M (3 ft) at 85° afforded pure **13:** λ_{max} (isooctane) 265 (ϵ 2740), 231 (1480), 225 (1680), and 218 nm (1720); ν_{max} (neat) 3030, 2955, 2830, 1193, 1080, 1025, 923, 778, 723, and 678 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.87 (s, 2, cyclobutenyl), 5.63–6.07 (m, 4, olefinic), and 3.48 (ABq, J_{AB} = 9.5 Hz, $\Delta\nu_{AB}$ = 47.6 Hz, 4, $-CH_2O-$).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 81.99; H, 7.09.

***N*-Methyl-5*H*,7*H*-1,4:4a,7a-diethenofuro[3,4-*d*]pyridazine-2,3(1*H*,4*H*)-dicarboximide (14).** A cold (−78°) magnetically stirred solution of pure **13** (4.0 g, 27.4 mmol) in 100 ml of acetone was treated dropwise with a solution of 3.1 g (27.4 mmol) of *N*-methyltriazolinedione in 40 ml of acetone. The resulting reddish-pink solution was warmed to ambient temperature, refluxed in the presence of a few milliliters of absolute ethanol, and then cooled to room temperature. After the removal of the solvents in vacuo, the light orange solid was dissolved in a minimal amount of chloroform and filtered through a silica gel column (chloroform elution) to afford 6.6 g (93%) of white solid, mp 191–196°. Further purification by recrystallization (chloroform–ether) afforded the analytical sample, mp 197.5–199°: ν_{max} (KBr) 2970, 2865, 1770, 1705, 1460, 1395, 1192, 1035, and 810 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.26 (dd, J = 4.5, 3 Hz, 2, olefinic), 6.06 (s, 2, cyclobutenyl), 4.88 (dd, J = 4.2, 3.3 Hz, 2, >CHN<), 3.82 (s, 4, $-CH_2O-$), and 3.02 (s, 3, $>NCH_3$).

Anal. Calcd for $C_{13}H_{13}N_3O_3$: C, 60.22; H, 5.05; N, 16.21. Found: C, 59.98; H, 5.06; N, 16.22.

Dihydro-*N*-methyl-3*H*-3a,8,4,7-ethanediylidene-1*H*-cyclobuta[*c*]furo[3,4-*d*]pyridazine-5,6(4*H*,6a*H*)-dicarboximide (15). A solution of **14** (2.0 g) in 300 ml of acetone–benzene (1:1) was irradiated through quartz under a nitrogen blanket with a 450-W Hanovia lamp filtered with a Corex filter for 2 hr. The solvents were removed in vacuo to furnish crude **15.** This procedure was repeated until 16 g of **14** had been irradiated. The crude **15** was chromatographed on neutral activity I alumina [petroleum ether–chloroform (3:1) elution] to afford after recrystallization (chloroform–ether) 9.3 g (58%) of white solid, mp 150–153°. Further recrystallization gave white crystals, mp 161.5–162.5° (preheated bath): ν_{max} (KBr) 3015, 2845, 1762, 1700, 1467, 1265, 900, and 763 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.03 (dd, J = 4.4, 2.2 Hz, 2, >CHN<), 3.85 (ABq, J_{AB} = 31.3 Hz, 4, $-CH_2O-$), 3.47–3.75 (br m, 2, methine), 3.07 (s, 3, $>NCH_3$), and 3.02–3.25 (m, 2, methine).

Anal. Calcd for $C_{13}H_{13}N_3O_3$: C, 60.22; H, 5.03; N, 16.21. Found: C, 60.11; H, 5.02; N, 16.18.

Hexahydro-*N*-methyl-2*H*,4H-cyclopropa[3′,4′]pentaleno[1′,6′:1,3,2]cyclopropa[1,2-*c*]furan-1,5-biimine-6,7-dicarboximide (16). A solution of recrystallized **15** (1.3 g, 5 mmol) in 160 ml of distilled and degassed dioxane containing 25.5 g (150 mmol) of silver nitrate in 40 ml of water was heated in a heavy wall sealed glass vessel at 130° (oil bath temperature) for 4 days in the dark. The cooled tube was carefully opened in a hood, and the mixture was diluted with an equal volume of 7 *N* aqueous ammonia, stirred, and filtered. The resulting clear yellow filtrate was concentrated to ca. 20 ml, extracted with chloroform (5 × 40 ml), and the combined chloroform extracts were washed with brine and dried. Removal of the solvent in vacuo afforded 1.1 g of a tan solid which was recrystallized from chloroform–ether to afford 0.84 g (65%) of white material, mp 187–190°. A small portion of **16** was further purified by recrystallization (chloroform–ether) to afford white crystals, mp 191–192° dec; ν_{max} (KBr) 2860, 2850, 1768, 1690, 1465, 1234, 1142, 1135, 1048, 1000, 942, 903, 800, 765, 676, and 540 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.06 (br t, J = 2.8 Hz, 2, >CHN<), 3.83 (ABq, J_{AB} = 9.2 Hz, $\Delta\nu_{AB}$ = 19.7 Hz, 4, $-CH_2O-$), 3.08 (s, 3, $>NCH_3$), and 1.84–2.22 (br m, 4, cyclopropyl).

Anal. Calcd for $C_{13}H_{13}N_3O_3$: C, 60.22; H, 5.05; N, 16.21. Found: C, 60.01; H, 5.07; N, 15.94.

2a,7b-Dihydro-5*H*,7*H*-pentaleno[1′,6′:1,3,2]cyclopropa[1,2-*c*]furan (17b) ⇄ 2,4,5a,5b,5c,5d-Hexahydrocyclopropa[3,4]pentaleno[1,6-*cd*]pyran (17a). A mixture of **16** (0.75 g, 2.9 mmol), 1.16 g (29 mmol) of sodium hydroxide, and 30 ml of degassed 2-propanol was refluxed for 1 hr under argon. The cooled (0°) mixture was acidified to pH 1 with 3 *N* hydrochloric acid, basified again to pH 8 by slow addition of 3 *N* aqueous ammonia, and diluted with 20 ml of pentane–methylene chloride (1:1). To this clear solution was added 2.52 g (20 mmol) of activated manganese dioxide in one portion, and stirring was continued at room temperature for 10 hr. After filtration, the clear filtrate was diluted with pentane, washed with water (3 × 40 ml), and dried by shaking with sodium chloride–anhydrous sodium sulfate (1:1). The excess solvent was carefully removed by atmospheric fractional distillation (argon purging of the solution), and the remaining clear liquid was purified by bulb-to-bulb transfer (10^{-3} Torr) at room temperature to afford **17** as a clear solid, 295 mg (70%): mp 23–25°; λ_{max} (isooctane) 242 nm (ϵ 2800) and 233 sh (2400); ν_{max} (neat) 2840, 1202, 1026, 912, 740, and 730 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.58 (dd, $J_{3,4}$ = $J_{6,7}$ = 5.2 Hz, $J_{4,5}$ = $J_{5,6}$ = 2 Hz, 2, H_4 and H_6), 5.26 (d, $J_{3,4}$ = $J_{6,7}$ = 5.2 Hz, 2, H_3 and H_7), 4.2 (ABq, J_{AB} = 9.5 Hz, $\Delta\nu_{AB}$ = 3.95 Hz, 4, $-CH_2O-$), 3.35 (dt, $J_{1,5}$ = 7.1 Hz, $J_{4,5}$ = $J_{5,6}$ = 2 Hz, 1, H_5), and 2.62 (d, $J_{1,5}$ = 7.1 Hz, 1); *m/e* (calcd 146.0732) 146.0733.

8-Oxa[4.3.2]propella-2,10-diene (19). A mixture of pure **12** (48.6 mg, 0.328 mmol), 4 ml of carbon tetrachloride, 58.7 mg (0.33 mol)

of recrystallized *N*-bromosuccinimide, and a few granules of azobisisobutyronitrile was placed in a preheated oil bath (100°) and refluxed under argon. After initiation, the mixture was heated for an hour, cooled, filtered, and the filtrate was concentrated in vacuo to afford a clear oil. The ^{1}H NMR spectrum showed a broad >CHBr absorption at δ 4.2–4.8. Without further purification, this oil was dissolved in 10 ml of anhydrous ether, to which was added 38 mg (1 mmol) of lithium aluminum hydride under argon. After refluxing this gray-white mixture overnight, it was cooled and quenched with a saturated sodium sulfate solution. The white salts were removed by filtration and leached with hot ether. The dried filtrate was concentrated in vacuo and subjected to preparative GLC on 8% Carbowax 20M (6 ft) at 130° to afford two components; the first (27%) compared exactly with **19** (GC retention time, ir, and ^{1}H NMR), while the second was unreacted **12.**

Hydrogenation of 17. A 110-mg sample (0.754 mmol) of **17** dissolved in 2 ml of anhydrous tetrahydrofuran was introduced via syringe into a hydrogenation flask containing 3 ml of the same solvent and 126 mg of prereduced 5% rhodium on carbon. After an uptake of ca. 2 equiv of hydrogen, 1 ml of glacial acetic acid was added, and the mixture was stirred for an additional 5 hr. After filtration, the filtrate was diluted with pentane, washed with water, saturated sodium bicarbonate solution, water, and brine, and dried. The solvent was removed by atmospheric distillation, and the residue was subjected to preparative GLC on 5% PMPE (five ring) at 115° to afford three major components. The first to elute (49%, t_{rel} = 22 min) was characterized as **21:** ν_{max} (neat) 3020, 2940, 2860, 1065, 1022, and 915 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 3.78 (ABq, J_{AB} = 8.7 Hz, $\Delta\nu_{AB}$ = 9.2 Hz, 4, $-CH_2O-$), 2.5–2.83 (br m, 1, methine), and 1.4–2.12 (series of multiplets, 9, methine and methylenes); *m/e* (calcd 150.1044) 150.1047.

The second component (45%, t_{rel} = 30 min) proved to be a white solid, mp 71–72°, and was identified as **22** by direct comparison with an authentic sample.

The third component (6%, t_{rel} = 38 min) was not isolated or characterized.

Tetrahydrotriquinacene (24). To an ice cold stirred solution of crude diol **23**[23] (2.3 g) in 20 ml of alcohol-free methylene chloride and 3.36 g (33.3 mmol) of triethylamine was added in four equal portions a solution of methane-sulfonyl chloride (3.24 g, 28.2 mmol) in an equal volume of methylene chloride. The resulting white mixture was stirred at 0° for 30 min and quenched with water and the organic phase was washed with 10% hydrochloric acid, saturated sodium bicarbonate, and brine and dried. After the solvent had been removed in vacuo, the yellow oil was crystallized from chloroform–ether to afford 2 g (49%) of dimesylate as white crystals, mp 111.5–112°.

To a slurry of lithium aluminum hydride (2.4 g, 62 mmol) in 50 ml of anhydrous ether was added a solution of this dimesylate (2.0 g, 6.2 mmol) in 15 ml of anhydrous tetrahydrofuran. After this mixture had been refluxed for 10–12 hr, it was cooled (0°) and quenched with a saturated sodium sulfate solution. The white salts were removed by filtration and leached with hot ether. After the dried solvent had been carefully removed by atmospheric fractional distillation, the residue was passed through a Florisil column (pentane elution) to afford, after the above work-up, a clear liquid. This liquid was subjected to preparatory GLC on 8% Carbowax 20M (6 ft) at 100° to afford **24** as the major component which was isolated in sufficient quantity for comparison with authentic material[24] and to use in the ozonolysis reaction.

***cis*-2,8-Bis(hydroxymethyl)bicyclo[3.3.0]octane (25).**[25] To a 50-ml three-necked flask equipped with a stopper, gas inlet tube, condenser, and magnetic stirrer was added 198 mg (1.48 mmol) of **24** in 20 ml of chloroform. After cooling the solution to −20°, ozone was bubbled through the solution until the appearance of a bluish color. The resulting turbid solution was purged with oxygen for 10 min and then diluted with 5 ml of 95% ethanol followed by a slurry of sodium borohydride (450 mg, 118 mmol) in 10 ml of 20% aqueous ethanol. Stirring was continued overnight, and the mixture was carefully hydrolyzed with 1 *N* hydrochloric acid and diluted with chloroform. The organic phase was washed with dilute hydrochloric acid, saturated sodium bicarbonate solution, and brine, dried, and evaporated to afford 130 mg of viscous oil. Back extraction of the salt-saturated aqueous phase with chloroform afforded another 100 mg of diol **25**, 230 mg total (91%): ν_{max} (neat) 3290 and 2900 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) (crude) 4.32 (br, 2, -OH), 3.74 (ABq, J_{AB} = 10 Hz, $\Delta\nu_{AB}$ = 6.9 Hz, 2, $-CH_2O-$), 3.62 (s, 2, $-CH_2O-$), and 0.98–2.78 (series of multiplets, 12, methines and methylenes).

Independent Preparation of 1,3,3a,4,5,5a,6,7,7a,7b-Decahydropentaleno[1,6-*cd*]pyran (22). To a solution of **25** (230 mg, 1.35 mmol) in 5 ml of pyridine was added 257 mg (1.35 mmol) of *p*-toluenesulfonyl chloride in one portion, and the solution was stirred magnetically for 24 hr under argon. The solution was quenched with water and diluted with chloroform, and the separated organic phase was washed with 1 *N* hydrochloric acid and brine and dried. Removal of the solvent in vacuo afforded crude monotosylate as an oil which was immediately dissolved in 40 ml of anhydrous tetrahydrofuran. To this solution was added 75.5 mg (1.79 mmol) of pentane-washed sodium hydride under argon, and the mixture was stirred at reflux overnight. The cooled, carefully quenched mixture was extracted several times with petroleum ether (30–60°), and the combined extracts were washed with brine and dried. Removal of the solvent in vacuo (no heat) afforded a yellow liquid which was filtered through a small Florisil column (pentane elution). The concentrated eluate was subjected to preparative GLC on 5% SE-30 (5 ft) at 130° to afford pure **22** (50 mg, 24%) as a white solid: mp 67–69°; ν_{max} (KBr) 2945, 2870, 2840, 1155, 1114, 867, and 742 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 3.85 (ABX, J_{AB} = 12 Hz, 4, $-CH_2O-$), 2.28–2.77 (br m, 2, methines), and 1.35–2.04 (m, 10, methines and methylenes).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 79.03; H, 10.44.

7-Chloro-8,11-dithia[4.3.3]propell-3-ene 8,8,11,11-Tetraoxide (27). To a solution of sublimed **26**[26] (1.98 g, 10 mmol) in 15 ml of carbon tetrachloride was added 1.4 g (10.5 mmol) of recrystallized *N*-chlorosuccinimide, and stirring was continued under nitrogen for 18 hr at room temperature. After filtration and solvent evaporation, the residue was diluted with 100 ml of ice-cold anhydrous ether and treated under nitrogen with a standardized ethereal solution containing 40.8 mmol of monoperphthalic acid. The room temperature solution was stirred for 5 hr, and the precipitated phthalic acid was removed by filtration and washed with chloroform. The filtrate was concentrated in vacuo, and the resulting solid was dissolved in chloroform. After washing this solution once with 0.5 *N* sodium hydroxide–brine (1:1) and drying, the solvent was removed in vacuo to afford 2.5 g (84%) of white solid: mp 260–275° dec (methylene chloride–ether); ν_{max} (CH_2Cl_2) 1340, 1325, and 1120 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.88 (br s, 2, olefinic), 5.5 and 4.9 (each is a singlet, 1, >CHCl), 3.1–3.9 (m, 6, $-CH_2SO_2-$), and 2.4–2.8 (br m, 4, allylic).

Anal. Calcd for $C_{10}H_{13}ClO_4S_2$: C, 40.47; H, 4.42; S, 21.61. Found: C, 40.45; H, 4.51; S, 21.23.

8-Thia[4.3.2]propella-3,10-diene 8,8-Dioxide (28). To a solution of **27** (0.82 g, 2.77 mmol) in 150 ml of cold (−70°) anhydrous tetrahydrofuran was added under nitrogen 1.24 g (11.1 mmol) of commercial powdered potassium *tert*-butoxide in one portion, and stirring was continued for 2 hr while the solution warmed to room temperature. The water quenched solution was diluted with an equal volume of 50% brine and extracted with pentane. The combined extracts were washed with brine, dried, and concentrated in vacuo. The residue was chromatographed on neutral activity 1 alumina (chloroform–ether elution) to afford 0.27 g (50%) of yellow solid, mp 105–108°. Recrystallization (methylene chloride–pentane) and sublimation [105° (25 mm)] afforded **28** as a white solid: mp 110–111°; ν_{max} CH_2Cl_2) 1305, 1130, and 1112 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.0 (s, 2, cyclobutenyl), 5.84 (m, 2, olefinic), 3.12 (ABq, J_{AB} = 14 Hz, $\Delta\nu_{AB}$ = 15.8 Hz, 4, $-CH_2SO_2-$), and 2.3 (br s, 2, allylic).

Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.17; S, 16.33. Found: C, 61.08; H, 6.24; S, 16.26.

8-Thia[4.3.2]propella-3,10-diene (29). To a slurry of 3.8 g (0.1 mmol) of lithium aluminum hydride in 125 ml of ice-cold anhydrous ether was added, under nitrogen, 1.96 g (10 mmol) of recrystallized **28** in one portion, and stirring at reflux was continued for 42 hr. After quenching the cooled (0°) mixture with a saturated sodium sulfate solution, the white salts were removed by filtration and leached with hot chloroform–ether. The combined solvents were dried and evaporated in vacuo to give an oil which, when stored in ether overnight at 0°, afforded 0.34 g of unreacted **28** and 1 g of crude sulfide. Kugelrohr distillation afforded 0.84 g (62% yield based on consumed **28**) of **29** as a clear liquid: bp 95° (4

mm); ν_{max} (neat) 3030, 2900, 2825, 895, 764, 730, and 680 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.7–5.81 (m, 2, olefinic), 5.76 (s, 2, cyclobutenyl), 2.54 (ABq, J_{AB} = 12.6 Hz, $\Delta\nu_{AB}$ = 5 Hz, 4, $-CH_2S-$), and 2.02–2.3 (m, 4, allylic); *m/e* (calcd 164.0660) 164.0662.

8-Thia[4.3.2]propella-2,4,10-triene (30). To a solution of **29** (5 g, 30.4 mmol) in 100 ml of cold (−70°) methylene chloride was slowly added, over a period of 5 hr, 30.4 mmol of bromine in methylene chloride was slowly added, over a period of 5 hr, 30.4 mmol of bromine in methylene chloride under nitrogen. Solvent removal in vacuo afforded a reddish viscous oil: δ_{Me_4Si} ($CDCl_3$) 6.03 (ABq, J_{AB} = 2.8 Hz, $\Delta\nu_{AB}$ = 13 Hz, 2, cyclobutenyl), 4.42–4.84 (br m, 2, >CHBr), and 1.9–3.0 (br m, 8, methylene); *m/e* (calcd 321.9028) 321.9032.

To a solution of this dibromide in 300 ml of dry hexamethylphosphoramide were added 12.8 g (0.304 mol) of lithium chloride and 22.5 g (0.304 mol) of lithium carbonate, and the stirred slurry was heated at 90° for 17 hr. After cooling, the slurry was diluted with water and extracted with pentane. The combined extracts were washed with brine, dried, and evaporated in vacuo (no heat). The residue was then chromatographed on neutral activity I alumina [pentane–ether (1:1) elution] to afford after solvent removal, 4 g (81%) of **30:** bp 96° (5 mm); λ_{max} (isooctane) 264 (ϵ 2520), 229 (2100), and 223 nm (2270); ν_{max} (neat) 3020, 2900, 2820, 1224, 1074, 1008, 765, 740, 691, and 650 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.91 (br t, J = 1.3 Hz, 4, olefinic), 5.74 (s, 2, cyclobutenyl), and 2.56 (ABq, J_{AB} = 12 Hz, $\Delta\nu_{AB}$ = 18.4 Hz, 4, $-CH_2S-$).

Anal. Calcd for $C_{10}H_{10}S$: C, 74.05; H, 6.22. Found: C, 73.65; H, 6.35.

***N*-Methyl-5*H*,7*H*-1,4:4a,7a-diethenothieno[3,4-*d*]pyridazine-2,3(1*H*,4*H*)-dicarboximide (31).** A solution of 3.5 g (21.6 mmol) of distilled **30** in 100 ml of cold (−70°) acetone was treated dropwise with a solution of 2.44 g (21.6 mmol) of *N*-methyltriazolinedione in 20 ml of the same solvent under nitrogen. The resulting reddish-pink solution was warmed to ambient temperature, refluxed in the presence of a few milliliters of absolute ethanol, and then cooled. Solvent removal in vacuo left a tan solid which was filtered through a silica gel column (chloroform elution) to afford 5.6 g (93%) of white solid, mp 227–228°. Recrystallization (chloroform–ether) furnished white needles: mp 227.5–228°; ν_{max} (KBr) 2930, 2920, 1775, 1710, 1460, 1394, 1190, 1000, 796, 789, 744, and 567 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.22 (dd, J = 4.6, 3.3 Hz, 2, olefinic), 5.94 (s, 2, cyclobutenyl), 4.77 (br t, J = 3.8 Hz, 2, >CHN<), 3.02 (s, 3, $>NCH_3$), and 2.87 (ABq, J_{AB} = 12 Hz, $\Delta\nu_{AB}$ = 37.8 Hz, 4, $-CH_2S-$).

Anal. Calcd for $C_{13}H_{13}N_3O_2S$: C, 56.72; H, 4.76; S, 11.62. Found: C, 56.38; H, 4.85; S, 11.34.

Dihydro-*N*-methyl-3*H*-3a,8,4,7-ethanediylidene-1*H*-cyclobuta[*c*]thieno[3,4-*d*]pyridazine-5,6(4*H*,6a*H*)-dicarboximide (32). A deaerated solution of **31** (2.0 g) in 300 ml of benzene–acetone (1:1) was irradiated through quartz with a 450-W Hanovia lamp fitted with a Corex filter for 2 hr under nitrogen. The solvents were removed in vacuo to afford crude **32.** This procedure was repeated until 7.3 g of **31** had been irradiated. The crude **32** was chromatographed on neutral activity I alumina [petroleum ether–chloroform (3:1) elution] to give 6.5 g (89%) of white solid, mp 175–180°. Further purification by recrystallization (chloroform-ether) afforded white crystals: mp 185–185.5°; ν_{max} (KBr) 2980, 1750, 1690, 1463, 1308, and 538 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 4.95 (dd, J = 4.6, 2.5 Hz, 2, >CHN<), 3.42–3.79 (br m, 2, methine), 3.07 (s, 3, $>NCH_3$), 2.92–3.07 (m, 2, methine), and 2.92 (s, 4, $-CH_2S-$).

Anal. Calcd for $C_{13}H_{13}N_3O_2S$: C, 56.72; H, 4.76; N, 15.27. Found: C, 56.41; H, 4.73; N, 15.13.

Hexahydro-*N*-methyl-2*H*,4*H*-cyclopropa[3′,4′]pentaleno[1′,6′:1,3,2]cyclopropa[1,2-*c*]thiophene-1,5-biimine-6,7-dicarboximide (33). A solution of recrystallized **32** (1.38 g, 5 mmol) in 160 ml of distilled and degassed dioxane containing 25.5 g (150 mmol) of silver nitrate in 40 ml of water was heated in a heavy wall sealed glass vessel at 130° (oil bath temperature) for 4 days in the dark. The cooled tube was carefully opened in a hood, and the mixture was diluted with an equal volume of 7 *N* aqueous ammonia, stirred, and filtered. The resulting clear yellow filtrate was concentrated to ca. 20 ml and extracted with chloroform (5 × 40 ml), and the combined chloroform extracts were washed with brine and dried. Removal of the solvent in vacuo afforded 1.2 g of yellow solid which was crystallized from chloroform–ether to furnish 0.85 g (62%) of white solid, mp 173–175°. Further recrystallization from chloroform–hexane afforded white needles, mp 175–176.5° dec; ν_{max} (KBr) 2920, 1763, 1700, 1468, 1396, 1232, 797, and 748 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.03 (br t, J = 3 Hz, 2, >CHN<), 3.08 (s, 7, $-CH_2S-$ and $>NCH_3$), 2.46 (d, J = 4 Hz, 1, cyclopropyl syn to sulfur ring), and 1.84–2.17 (br m 3, cyclopropyl).

Anal. Calcd for $C_{13}H_{13}N_3O_2S$: C, 56.72; H, 4.76; N, 15.27. Found: C, 56.64; H, 4.74; N, 15.22.

2a,7b-Dihydro-5*H*,7*H*-pentaleno[1′,6′:1,3,2]cyclopropa[1,2-*c*]thiophene (34b) ⇄ 2,4,5a,5b,5c,5d-Hexahydrocyclopropa[3,4]-pentaleno[1,6-*cd*]thiopyran (34a). A mixture of **33** (0.75 g, 2.73 mmol), 1.09 g (27.3 mmol) of sodium hydroxide, and 30 ml of degassed 2-propanol were refluxed for 1 hr under argon. The cooled (0°) mixture was acidified to pH 1 with 3 *N* hydrochloric acid, basified again to pH 8 by slow addition of 3 *N* aqueous ammonia, and diluted with 20 ml of pentane–methylene chloride (1:1). To this clear solution was added 2.37 g (27.3 mmol) of activated manganese dioxide in one portion, and stirring was continued at room temperature for 6 hr. After filtration, the clear filtrate was diluted with pentane, washed with water (3 × 40 ml), and dried by shaking with sodium chloride–anhydrous sodium sulfate (1:1). The excess solvent was carefully removed by atmospheric fractional distillation (argon purging of the solution), and the remaining clear liquid was purified by bulb-to-bulb transfer (10^{-3} Torr) at 50° to afford **34** as a clear liquid, 193 mg (44%): λ_{max} (isooctane) 240 nm (ϵ 1900); ν_{max} (neat) 3040, 2910, 2840, 1362, 748, 738, and 717 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) (40°) 5.22–5.41 (m, 4, olefinic), 3.4 (ABq, J_{AB} = 11.8 Hz, $\Delta\nu_{AB}$ = 7.9 Hz, 4, $-CH_2S-$), 3.18–3.4 (m, 1, H_5), and 2.98 (d, J = 6.8 Hz, 1, H_1); *m/e* (calcd 162.0503) 162.0506.

1a,2,7,7a-Tetrahydro-*N*-phenyl-1,2a,6a-metheno-1*H*-cyclopropa[*b*]naphthalene-2,7-biimine-8,9-dicarboximide (36).[27] To a magnetically stirred solution of **35**[12] (105 mg, 0.315 mmol) in 50 ml of dichloromethane at −78° was added dropwise, during 5 min, a solution of bromine (50.4 mg, 0.315 mmol) in 10 ml of carbon tetrachloride. Upon completion of the addition, the solution was stirred for 15 min and allowed to warm to room temperature for 1 hr. The clear yellow solution was evaporated in vacuo to leave 155 mg (100%) of dibromide as a white crystalline solid: δ_{Me_4Si} ($CDCl_3$) 7.40 (m, 5, aryl), 4.95 (m, 2, >CHN<), 4.33 (m, 2, >CHBr), and 1.9–3.1 (br m, 8, cyclopropyl and methylene).

A magnetically stirred solution of this dibromide (751 mg, 1.53 mmol) in dry tetrahydrofuran (30 ml) under nitrogen was treated with 1,5-diazabicyclo[5.4.0]undecene (900 mg, 6 mmol) and heated at 50° for 12 hr. Hydrolysis was accomplished by the addition of water (5 ml) and stirring for 30 min. The solution was diluted with 150 ml of ether, and the organic phase was washed with water, 5% hydrochloric acid solution (3x), water, and brine. After drying and solvent removal, there was obtained 497 mg (98.6%) of **36.** Chromatography on alumina and elution with 5% chloroform–benzene gave pure **36** as a colorless solid, mp 182.5–183.0° (from acetone–ether); δ_{Me_4Si} ($CDCl_3$) 7.37 (m, 5, aryl), 6.10 (AA′BB′ pattern, 4, olefinic), 5.20 (m, 2, >CHN<), and 1.92–2.60 (m, 3, cyclopropyl), and 0.56 (d, J = 4 Hz, 1, cyclopropyl); *m/e* (calcd 329.1164) 329.1174.

Anal. Calcd for $C_{20}H_{15}N_3O_2$: C, 72.94; H, 4.59; N, 12.76. Found: C, 72.91; H, 4.63; N, 12.75.

Ozonolysis of 36. Into a 1 l. three-necked round-bottomed flask equipped with a stopper, a condenser with gas outlet, and a bubbler inlet was placed 3.43 g (10.4 mmol) of **36** in 500 ml of chloroform. This solution was cooled in ice, while a stream of ozone was introduced, until a slight blue color persisted. Excess ozone was purged with oxygen (10 min), ethanol (80 ml) was added to aid solubility, and a solution of sodium borohydride (4.00 g, 106 mmol) dissolved in 20% aqueous ethanol was added dropwise to the cooled reaction mixture. After 12 hr, 10% hydrochloric acid was added (to pH 4), the layers were separated, and the organic layer was washed with 10% hydrochloric acid and saturated sodium bicarbonate solutions. These washings were reextracted with chloroform, and the combined organic phases were washed with brine, dried, and evaporated to yield 2.95 g (84%) of white crystalline diol **37a:** ν_{max} (KBr) 3420, 1750, and 1685 cm^{-1}; δ_{Me_4Si} (py-d_5) 7.1–7.4 (m, 5, aryl), 5.55 (s, 2, –OH), 5.30 (pseudo t, 2, >CHN<), 3.90 (s, 4, $-CH_2OH$), and 1.80–2.10 (m, 4, cyclopropyl).

A 250-mg (0.74 mmol) sample of this impure diol was dissolved in purified pyridine (25 ml) and treated with acetic anhydride (465 mg, 4.36 mmol). The solution was stirred overnight and evaporated to dryness in vacuo. There was obtained 190 mg (61%) of di-

acetate **37b**; mp 170.2–170.5° (from 2-propanol); δ_{Me_4Si} ($CDCl_3$) 7.50 (m, 5, aryl), 5.15 (m, 2, >CHN<), 4.20 (ABq, J = 12.5 Hz, $\Delta\nu_{AB}$ = 26.9 Hz, 4, $-CH_2O-$), 2.17 (m, 4, cyclopropyl), and 1.94 (s, 6, methyl).

Anal. Calcd for $C_{22}H_{21}N_3O_6$: C, 62.41; H, 5.00; N, 9.92. Found: C, 62.26; H, 4.96; N, 9.87.

Hexahydro-*N*-phenyl-2*H*,4*H*-cyclopropa[3′,4′]pentaleno[1′,6′:1,3,2]cyclopropa[1,2-*c*]furan-1,5-biimine-6,7-dicarboximide (38). A solution of 75 mg (0.22 mmol) of unpurified **37a** in 15 ml of freshly distilled pyridine was heated at reflux for 2 hr with 54.1 mg (0.274 mmol) of *p*-toluenesulfonyl chloride. The solution was cooled, acidified to pH 2 with 5% hydrochloric acid, and extracted with chloroform (5 × 25 ml). The usual work-up afforded a tan-colored oil (>100%), thin layer chromatography of which indicated two major products, one of which was subsequently shown to be **38**.

A solution containing 250 mg (0.74 mmol) of impure **37a** and 180.5 mg (0.945 mmol) of *p*-toluenesulfonyl chloride in 25 ml of anhydrous pyridine was stirred overnight at 25°. Removal of solvent in vacuo left a solid residue which was taken up in anhydrous tetrahydrofuran (25 ml). Sodium hydride (36.1 mg, 0.756 mmol) was added in portions, and the mixture was stirred at 25° (3 hr) before heating to reflux (45 min). Water was carefully added, and the mixture was extracted with chloroform (5 × 50 ml). Work-up afforded a brown semisolid which when chromatographed on Florisil gave 37.8 mg of **38**: mp 219.5–220.0° (from 2-propanol); δ_{Me_4Si} ($CDCl_3$) 7.25–7.60 (m, 5, aryl), 5.15 (pseudo t, 2, >CHN<), 3.88 (ABq, J = 9.0 Hz, $\Delta\nu$ = 18.3 Hz, 4, $-CH_2O-$), and 1.9–2.2 (m, 4, cyclopropyl); *m/e* (calcd 321.1113) 321.1118.

Anal. Calcd for $C_{18}H_{15}N_3O_3$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.13; H, 4.71; N, 12.73.

Dimesylate 39. To a solution of impure **37a** (280 mg, 0.825 mmol) in 25 ml of dichloromethane was added 250 mg of purified triethylamine followed by cooling to −10° and dropwise introduction of methanesulfonyl chloride (209 mg, 1.82 mmol). After 15 min, the organic phase was washed with ice water, cold 5% hydrochloric acid, cold saturated sodium bicarbonate solution, and brine. From the dried dichloromethane solution, there was isolated 399 mg (87%) of **39** as a white solid: mp 214.7–215.0° (from tetrahydrofuran–ether–hexane); δ_{Me_4Si} ($CDCl_3$) 7.2–7.5 (m, 5, aryl), 5.15 (pseudo t, 2, >CHN<), 4.30 (s, 4, $-CH_2O-$), 3.00 (s, 6, methyl), and 1.8–2.3 (m, 4, cyclopropyl); *m/e* (calcd 495.077) 495.076.

Anal. Calcd for $C_{20}H_{21}N_3O_8S_2$: C, 48.48; H, 4.27; N, 8.48. Found: C, 48.29; H, 4.33; N, 8.21.

Hexahydro-3-benzyl-*N*-methyl-2*H*,4*H*-cyclopropa[3′,4′]pentaleno[1′,6′:1,3,2]cyclopropa[1,2-*c*]pyrrole-1,5-biimine-6,7-dicarboximide (40).[28] A solution of 570 mg (1.15 mmol) of dimesylate **39** and 400 mg (3.74 mmol) of freshly distilled benzylamine in 75 ml of acetonitrile was stirred at ambient temperature under nitrogen for 14 hr. The solution was evaporated to give a yellow oil which, after chromatography on silica gel (elution with ether), yielded 296 mg (63%) of **40** as a white solid, mp 158.3–158.5° (from tetrahydrofuran–ether): ν_{max} ($CHCl_3$) 3030, 2920, 2800, 1765, 1745, 1700, 1505, and 1410 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.45 and 7.20 (m, 10, aryl), 5.02 (m, 2, >CHN<), 3.53 (s, 2, benzyl), 2.59 (ABq, J_{AB} = 9.4 Hz, $\Delta\nu_{AB}$ = 37.4 Hz, 4, $-CH_2N<$), 2.43 (m, 1, cyclopropyl syn to nitrogen ring), and 1.95 (m, 3, cyclopropyl).

Anal. Calcd for $C_{25}H_{22}N_4O_2$: C, 73.15; H, 5.40; N, 13.65. Found: C, 72.94; H, 5.48; N, 13.53.

***N*-Benzyl-2a,7b-dihydro-5*H*,7*H*-pentaleno[1′,6′:1,3,2]cyclopropa[1,2-*c*]pyrrolidine (41b) ⇄ *N*-Benzyl-2,4,5a,5b,5c,5d-hexahydrocyclopropa[3,4]pentaleno[1,6-*cd*]piperidine (41a).** All solutions and solvents were degassed prior to use, and exposure to the atmosphere was minimized.

A stirred mixture of 324.4 mg (0.792 mmol) of **40**, 316.8 mg (7.92 mmol) of sodium hydroxide, and 20 ml of 2-propanol was refluxed for 1 hr under argon. The milky yellow solution was cooled to 0°, acidified to pH 6 with 50% aqueous acetic acid, basified (pH 9) with 3 *N* ammonium hydroxide, and diluted with 20 ml of pentane. To this clear, yellow solution was added, in one portion, 688 mg (7.92 mmol) of activated manganese dioxide,[29] and stirring was continued at ambient temperature for 9 hr. After filtration, the clear, yellow filtrate was diluted with pentane, rinsed with water (4 × 10 ml), and dried by shaking with sodium chloride–sodium sulfate. Excess solvent was carefully distilled utilizing argon bubbling. The concentrated solution was transferred to a sublimator, and the remaining solvent was distilled at high vacuum. Sublimation [40–95° (1.2 × 10^{-3} Torr)] gave 100 mg (54%) of **41** as low melting (ca. 10°) white solid: λ_{max} (isooctane) 215 nm (ε 6700), 231 (ε 5000), 241 sh (ε 2800), and 252 sh (ε 1600); ν_{max} (neat) 3055, 3045, 2945, 2890, 2800, 2765, 1735, 740, 715, and 695 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 7.32 (m, 5, aryl), 5.53 (dd, $J_{3,4}$ = $J_{6,7}$ = 5 Hz, $J_{4,5}$ = $J_{5,6}$ = 2 Hz, 2, H_4 and H_6), 5.29 (d, $J_{3,4}$ = $J_{6,7}$ = 5 Hz, 2, H_3 and H_7), 3.75 (s, 2, benzyl), 3.26 (dt, $J_{1,5}$ = 6.5 Hz, $J_{4,5}$ = $J_{5,6}$ = 2 Hz, 1, H_5), 3.18 (ABq, J_{AB} = 9.0 Hz, $\Delta\nu_{AB}$ = 49.6 Hz, 4, $-CH_2N<$), and 2.98 (d, $J_{1,5}$ = 6.5 Hz, 1, H_1); *m/e* (calcd 235.1361) 235.1355.

Hexahydro-*N*-methyl-2*H*,4*H*-cyclopropa[3′,4′]pentaleno[1′,6′:1,3,2]cyclopropa[1,2-*c*]thiophene-1,5-biimine-6,7-dicarboximide 3,3-Dioxide (42). A solution of 730 mg (4.2 mmol) of purified *m*-chloroperbenzoic acid in 5 ml of chloroform was added dropwise to a stirred ice-cold solution of **32** (550 mg, 2.0 mmol) in 25 ml of chloroform. The clear solution was diluted to 50 ml with chloroform, washed with 0.5 *N* sodium hydroxide–brine solution (1:1), and dried. Evaporation in vacuo afforded a light yellow solid which was crystallized from chloroform–ether to afford 500 mg (82%) of white crystals, mp 189–190° dec; ν_{max} (KBr) 2990, 2930, 1763, 1695, 1462, 1318, 1300, 1155, 1135, and 470 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.11 (t, J = 2.5 Hz, 2, >CHN<), 3.38 (ABq, J_{AB} = 15 Hz, $\Delta\nu_{AB}$ = 41 Hz, 4, $-CH_2SO_2-$), 3.04 (s, 3, $>NCH_3$), and 1.99–2.44 (br m, 4, cyclopropyl).

Anal. Calcd for $C_{13}H_{13}N_3O_4S$: C, 50.81; H, 4.26; N, 13.68. Found: C, 50.60; H, 4.45; N, 13.41.

Attempted Preparation of 43. A mixture of **42** (500 mg, 1.63 mmol), 650 mg (16.3 mmol) of sodium hydroxide, and 20 ml of degassed 2-propanol was refluxed for 1 hr under argon. The cooled (0°) mixture was acidified to pH 1 with 3 *N* hydrochloric acid, basified again to pH 8 by slow addition of 3 *N* aqueous ammonia, and diluted with 20 ml of ether. To this clear solution was added 1.4 g (16.3 mmol) of activated manganese dioxide in one portion, and stirring was continued at room temperature for 10 hr. After filtration, the clear filtrate was diluted with pentane, washed with water (4 × 30 ml), and dried by shaking with sodium chloride–anhydrous sodium sulfate (1:1). The excess solvent was carefully removed by fractional distillation such that the pot temperature never exceeded 25° (argon purging of the solution), and the remaining yellow liquid was transferred to a sublimation apparatus. Sublimation at room temperature (10^{-5} Torr; Dry Ice cold finger) afforded 125 mg (59%) of **126** as a white solid: mp 0–1°; λ_{max} (isooctane) 219 (ε 26,000) and 250 sh nm (6400); ν_{max} (neat) 3080, 3055, 2880, 1640, 892, 865, and 823 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 6.02 (br s, 4, olefinic), 5.02 (d, J = 1.4 Hz, 2, exomethylene), 4.96 (d, J = 1.8 Hz, 2, exomethylene), 4.02 (d, J = 6 Hz, 1, H_5), and 3.82 (m, 1, H_1); *m/e* (calcd 130.0782) 130.0785.

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References and Notes

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Alkylation of Benzene with Isoparaffin–Alkyl Chloride Mixtures[1]

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Abstract: The product formed by the alkylation of benzene with *tert*-butyl chloride at room temperature in the presence of an isoparaffin and aluminum chloride consists not only of *tert*-butylbenzene but also of alkylbenzene in which the alkyl group is produced from the isoparaffin. For example, the gradual addition of *tert*-butyl chloride to a stirred mixture of benzene, isopentane, and the catalyst yields chiefly pentylbenzenes during the early part of the experiment; the relative quantity of *tert*-butylbenzene increases as the addition proceeds. On the other hand, when a secondary alkyl chloride, isopropyl chloride, is reacted with benzene and isopentane, isopropylbenzene is the chief product, pentylbenzenes being formed in only minor amount. Alkylation of benzene by saturated hydrocarbons does occur even with a primary alkyl chloride if it isomerizes readily to a tertiary chloride (1-chloro-3,3-dimethylbutane) or yields a very active primary cation (benzyl chloride). The reaction mechanism and the reasons for the differences between the types of alkyl chlorides are discussed.

The aluminum chloride catalyzed alkylation of aromatic hydrocarbons with alkyl chlorides has been intensively investigated since Friedel and Crafts first reported that pentylbenzene is formed by the action of aluminum chloride on a solution of pentyl chloride in benzene.[2] It is the purpose of the present paper to show the marked effect on the course of the reaction of paraffins and cycloparaffins which contain tertiary carbon atoms. The literature does contain some examples of the reaction of benzene with isoparaffins and alkylcycloparaffins during its alkylation with olefins[3,4] or *tert*-alkyl fluorides,[5] but the reactions are not adequately discussed.

The product formed by the alkylation of benzene with *tert*-butyl chloride at room temperature in the presence of aluminum chloride and a saturated hydrocarbon containing a tertiary carbon atom consists not only of the expected *tert*-butylbenzene, but also of the alkylbenzene isomers produced by alkylation of the benzene with a moiety derived from the saturated hydrocarbon. Thus, the dropwise addition of *tert*-butyl chloride to a stirred mixture of benzene, isopentane, and aluminum chloride at room temperature (expt 1) resulted in the formation of isobutane and of liquid product containing approximately equal amounts of *tert*-butylbenzene and pentylbenzenes (chiefly the *sec*-isopentyl isomer, 2-methyl-3-phenylbutane). The pentylbenzenes were the principal products during the early part of the experiment; the relative quantity of *tert*-butylbenzene increased as the experiment proceeded, presumably because the relative proportion of available isopentane decreased. The final liquid product contained approximately equal quantities of *tert*-butylbenzene and the pentylbenzenes.

The reaction may be explained by the following pathway, which involves hydride transfer (hydrogen–chlorine exchange):