

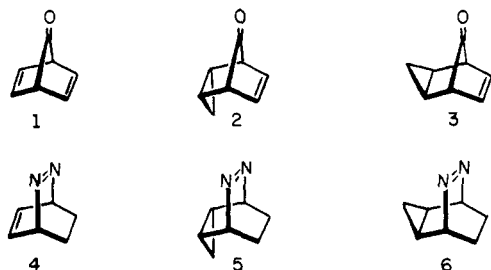
Cheletropic $\sigma_{2s} + \sigma_{2s} + \sigma_{2s}$ Ejection of Nitrogen from 9,10-Diazasnoutenes as a Route to Monofunctionalized Semibullvalenes. Ground State Substituent Effects on Equilibrium Displacements

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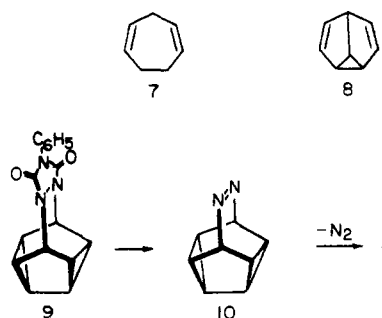
Abstract: The two-step reaction sequence of alkaline hydrolysis followed by air or manganese dioxide oxidation provides a convenient synthetic method for transforming urazole-blocked 9,10-diazasnoutanes to 9,10-diazasnoutenes. These end products are very labile and nonisolable, decomposing very readily by symmetry allowed cheletropic loss of nitrogen to the corresponding semibullvalenes. A series of these highly fluxional compounds has been prepared having a functional group at C₁(C₅), C₂(C₄), or C₃. The first two types of semibullvalenes are of particular interest because they are capable of providing direct information on the question of ground state equilibrium imbalances in twofold degenerate systems. Since inherent thermodynamic weighting toward one of the constituent isomers does not prevail *a priori* in the parent hydrocarbon, it becomes possible to assess the direction of perturbational effects arising from the various modes of framework substitution. However, because of the low activation energy to Cope rearrangement in these semibullvalenes, recourse to an approximation method of analysis of the low-temperature pmr spectra was required. Notwithstanding, the results clearly indicate decided preferential attachment to olefinic > cyclopropyl > aliphatic, irrespective of the nature and location of the R group.

The study of cheletropic reactions has in recent years provided chemists with much fundamental information about such fragmentation processes.^{2,3} In particular, findings relating to those structural features inherently conducive to facile ejection of gaseous by-product (CO, N₂, SO₂, etc.) have led to the development of a comprehensive electronic picture of the rate-determining bond fission. The ready thermal decarbonylation of norbornadien-7-one (**1**) which has precluded all attempts at its isolation,⁴ the rapid conversion of *endo*-tricyclo[3.2.1.0^{2,4}]octen-8-one (**2**) to cycloheptatriene at 30–40°,^{5–7} and the unreactivity of *exo* isomer **3** under comparable conditions (loss of CO occurs at measurable rates only at 110–150°)^{6,7} are illustrative of the stereoelectronic effects which have excited attention. Analogously, azo compound **4** readily decomposes to 1,3-cyclohexadiene at –78°,⁸ and **5** suffers loss of nitrogen 10¹⁷ times faster than 2,3-diazabicyclo[2.2.2]oct-2-ene,⁹ but a change in the dihedral angle relationship of the cyclopropane ring and the departing group leads again to substantial amelioration of cheletropic reactivity, derivatives of **6** requiring temperatures of 160–190° to extrude nitrogen.^{10,11} The reactivity levels of **1**, **2**, **4**, and **5** are such as to support the proposal that orbital symmetry-allowed concerted cycloreversions operate in these examples, as opposed to the disallowed and consequently probably stepwise decompositions of **3** and **6**.



In design, our synthetic approach to the semibullvalene nucleus was founded upon the dramatically enhanced decomposition rate of **5** and an awareness that loss of nitrogen in this instance leads to 1,4-cycloheptadiene (**7**). The structural similarity of **7** and semibullvalene (**8**) is obvious, and

the utilization of an azo functional group to introduce the two sites of unsaturation in the final step under very mild conditions was particularly attractive in view of the high chemical reactivity of this hydrocarbon. In the preceding paper,¹² the simple and relatively rapid construction of **9** and several monosubstituted derivatives of this penultimate precursor to elusive functionalized semibullvalenes was detailed. Our attention is focused herein on the efficient hydrolysis-oxidation of **9** to **10** and cheletropic decomposition of the latter. In this connection, the thermal stability of **10**



was expected to be even less than that of **5** in view of its more highly strained nature. Furthermore, this azo compound is so constructed that the nitrogen molecule must depart in a direction syn to the fragmenting σ bond of one of the cyclopropane rings, *i.e.*, that stereoelectronic condition particularly favorable for the concerted retrograde homo Diels-Alder mechanism.¹³ In fact, the alignment of the σ electrons taking part in the $\sigma_{2s} + \sigma_{2s} + \sigma_{2s}$ bond reorganization approximates very closely what may be considered the ideal geometry.^{14,15} Also, owing to the inherent symmetry of **10** (and the fluxional nature of **8**), its conversion to semibullvalene is independent of which proximate edge cyclopropyl bond experiences simultaneous fission.

Results

Hydrolysis Experiments. Preparation of the semibullvalenes required vigorous hydrolysis of the urazole ring in those 9,10-diazasnoutane precursors of general formula **9** under conditions where the liberated hydrazo compound would not suffer concomitant oxidation. In the latter event,

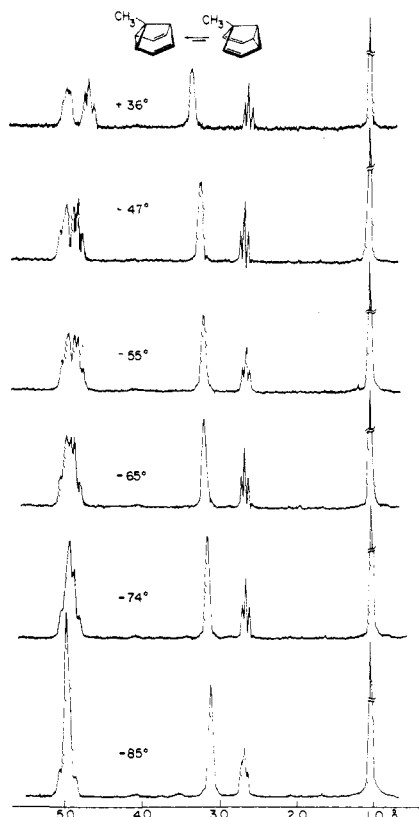
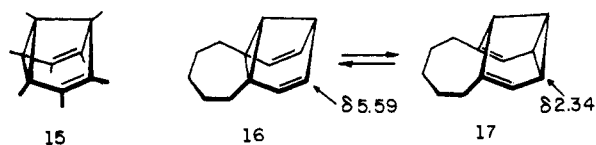


Figure 1. Selected variable-temperature pmr spectra of 1(5)-methylsemibullvalene (60 MHz, CS_2 solution).



mulas) may not correspond as closely as desired to the true values (were they obtainable) in **13a** and **14a**.^{31,32} Consequently, this method is only approximative and, of course, acquires less validity as the substituent deviates increasingly from one of purely aliphatic character. With these reservations in mind, the chemical shift data³³ at -85° and $+36^\circ$ suggest the mole fraction of **13a** to be 83 and 75%, respectively, with the consequence that $K_{-85^\circ} = 4.9$ ($\Delta G^\circ = 595$ cal/mol) and $K_{+36^\circ} = 3.0$ ($\Delta G^\circ = 675$ cal/mol).³⁴

Comparable hydrolytic treatment of **12b** gave **13b** \rightleftharpoons **14b** in 76% yield as a colorless oil which solidified below 0° subsequent to vpc purification. Its 100-MHz pmr spectrum at $+33^\circ$ in CD_2Cl_2 shows, in addition to the aromatic multiplet of area 5 centered at δ 7.10 due to the phenyl substituent, signals corresponding to pairs of protons at δ 5.43 (m, H_4 and H_6), 5.21 (m, H_3 and H_7), and 3.43 (m, H_2 and H_8), and an upfield triplet ($J_{4,5} = 2.5$ Hz) easily recognized as H_5 (see Figure 2). Saturation of the δ 5.43 multiplet was unique in causing collapse of this triplet to a singlet; the location of the H_4, H_6 absorption was thereby established. The temperature-invariant characteristics of the δ 5.21 signal denote it as arising from H_3 and H_7 . Thus, the set of peaks at δ 3.43 must be assigned to H_2, H_8 , this spectral feature demanding that **13b** dominate the equilibrium. This analysis is supported by the low-temperature pmr spectra of the phenylsemibullvalene which reveal behavior similar to the 1(5)-methyl derivative, namely, the H_2, H_8 signal shifting to higher field (δ 3.22 at -126°) and the H_4, H_6 multiplet to lower field (5.69 at -126°). Given the earlier reservations concerning the applicability of eq 1, the conclusions

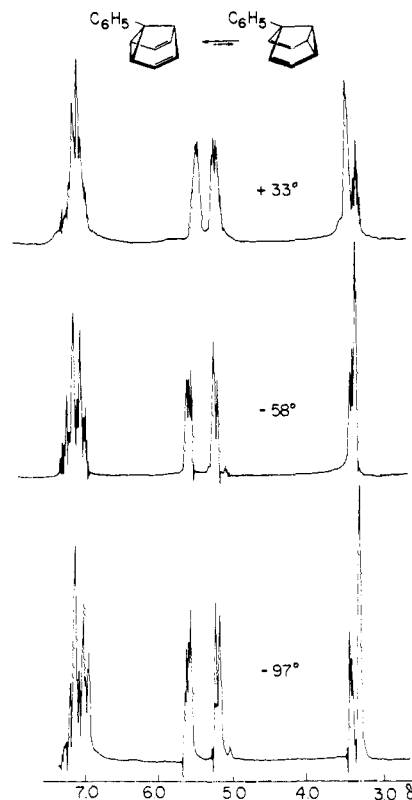


Figure 2. Selected variable-temperature pmr spectra of 1(5)-phenylsemibullvalene (100 MHz, CD_2Cl_2 -Freon 11 solution (1:1)).

to be drawn from these experiments are that **13b** is favored to an extent of approximately 95% at room temperature,³³ and that the equilibrium is weighted virtually completely in this direction at -126° . The close correspondence of the relevant chemical shifts of **13b**, **16**, and **17** at the low temperatures is particularly noteworthy.

1(5)-Methoxymethylsemibullvalene (**13c** \rightleftharpoons **14c**), obtained in 39% yield from **12c** after vpc purification, also displays a pmr spectrum (60 MHz) with several interesting features. For example, the prevailing equilibrium conditions are such at $+38^\circ$ that the peaks due to the permanently olefinic protons (H_3, H_7) and those at the terminus of the divinylcyclopropane unit (H_4, H_6) overlap to give a quite narrow multiplet centered at δ 5.12. The signals due to H_2, H_8 and the $-\text{OCH}_2-$ protons are similarly superimposed with the result that a broadened singlet is seen at δ 3.35. The remainder of the spectrum is comprised of a three-proton singlet at δ 3.20 and the characteristic H_5 multiplet at δ 3.04. As the temperature is gradually lowered to -119° , chemical shift changes expectedly take place, the H_4, H_6 and H_2, H_8 multiplets (assignments based on spin decoupling studies effected under the conditions of the experiment) now appearing at δ 5.45 and 3.10, respectively, in regions free of other peaks. These data signify an increase in the equilibrium concentration of **13c** over this temperature range of approximately 10% (86% \rightarrow 96%).³³

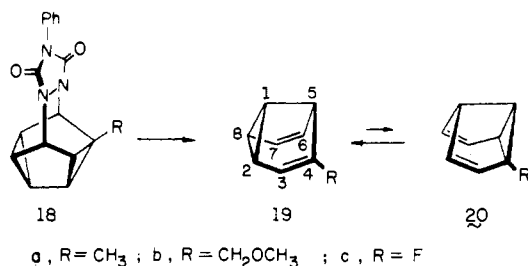
Hydrolysis-oxidation (necessarily O_2 ; MnO_2 promoted product decomposition) of **12d**-OAc furnished alcohol **13d** \rightleftharpoons **14d** (54%) which because of its thermal sensitivity was purified by preparative thick-layer chromatography on silica gel. The resulting oil was identified on the basis of its mass spectral molecular ion (m/e 134.0733) and pmr spectrum at 35° , the features of which are very similar to those of **13c** \rightleftharpoons **14c** (see Experimental Section).

2(4)-Substituted Semibullvalenes. In contrast to the C_s symmetry inherent in 1(5)-substituted semibullvalenes,



Figure 3. Selected variable-temperature pmr spectra of 2(4)-methylsemibullvalene (60 MHz; C_2Cl_4 solution at 80 and 99°; CS_2 solution at 42° and below).

those possessing an R group at $C_2(C_4)$ lack a necessary σ plane. In the latter examples, however, the pairs of valence isomeric structures differ intrinsically in their total number of olefinic protons. Pmr analysis is thereby greatly facilitated, since simple integration techniques now suffice for determining the favored equilibrium direction.



Application of the now conventional hydrolytic procedure to **18a** afforded **19a** \rightleftharpoons **20a** in 52% purified yield. Selected 60-MHz pmr spectra recorded at several temperatures from +99 to -101° are shown in Figure 3. It will be noted that at +42° the signals arising from H_2, H_8 overlap those due to H_1, H_5 and form a narrow multiplet at δ 2.93. The peaks for H_6 and H_7 are also coalesced (δ 5.19) but distinct from H_3 (δ 4.84) which is proximal to the methyl group. In contrast, each individual proton except the H_2, H_8 pair emerges as a well-defined signal at -101° . Double resonance experiments at this temperature confirmed the individual assignments and led to determination of many coupling constants.

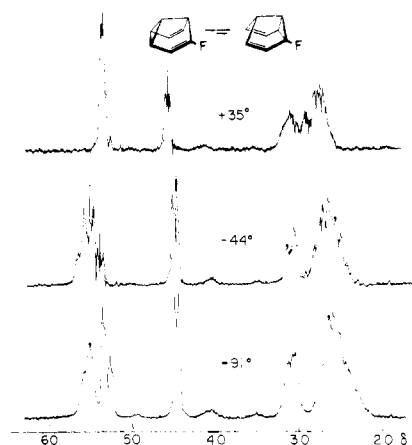


Figure 4. Selected variable-temperature pmr spectra of 2(4)-fluorosemibullvalene (60 MHz, CS_2 solution).

The presence of only three olefinic protons is patently evident. Fitting of these chemical shift data to eq 1 denotes that isomer **19a** is present to the extent of approximately 95% at -101° . Analogous computations based upon the spectrum recorded at +42° suggest that the concentration gradient of less favored cyclopropyl substituted isomer **20a** increases roughly to the 13–18% level at this temperature.

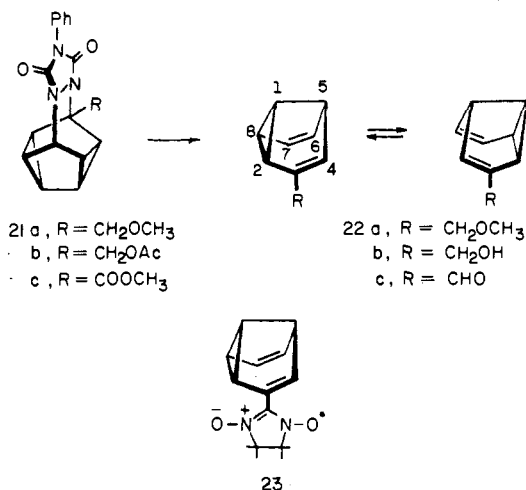
A strikingly similar example of heavily favored bonding to sp^2 hybridized carbon was noted also for the isomeric methoxymethylsemibullvalenes **19b** \rightleftharpoons **20b**. The assignment of **19b** as the major constituent in solution is firmly based upon the pmr spectrum (30°) which reveals three well-separated olefinic proton multiplets centered at δ 5.28, 5.12, and 4.73, in addition to the pairs of cyclopropyl (δ 3.76 and 3.72) and bridgehead hydrogens (δ 3.13 and 3.07) which in this instance were of sufficiently different chemical shift at room temperature to be individually distinguishable (spin decoupling). In line with preceding findings, cooling of these solutions to low temperatures led to an enhancement in the relative amount of **19b**. However, the changes in signal positions were of a low order. Thus, H_6 shifted only from δ 4.73 to 4.79 and H_8 from δ 3.76 to 3.71 over this 130° temperature range.

9,10-Diazasoutane **18c** gave 2(4)-fluorosemibullvalene (**19c** \rightleftharpoons **20c**) in 71.5% yield under analogous conditions. From the variable-temperature pmr spectra (Figure 4), it is readily apparent that **19c** comprises again the thermodynamically favored structural arrangement. At +35° in CS_2 solution, the fluorocarbon displays a broad multiplet centered at δ 2.84 assignable to the pseudo-cyclopropyl protons, a second multiplet due to H_5 at δ 3.17, and two sets of olefinic multiplets at δ 4.62 (H_3) and 5.41 (H_6 and H_7). Gradual lowering of the temperature leads to decoalescence of H_6 and H_7 , but the upfield absorption, in contrast, remains a broad signal throughout the range examined.

Whereas synthetic access to the methyl, methoxymethyl, and fluoro derivatives was achieved without complication, all attempts to successfully hydrolyze **18-C₆H₅** and **18-CN** have failed. Insoluble orange-colored polymers were invariably obtained, the prospect of isolating the phenyl- and cyanosemibullvalenes being apparently undermined by an instability under the reaction conditions which frustrates their isolation.

3-Substituted Semibullvalenes. Those semibullvalenes which are derivatized at C_3 are distinctive in that the attachment of an R group at this permanently trigonal center does not lead to an equilibrium imbalance. Consequently, no information on ground state energy preferences can be acquired from this group of compounds. However, this

unique feature could in principle lend itself to a quantitative assessment of the still unknown degenerate semibullvalene isomerization rate. As Ullman has suggested,³⁵ were nitronyl nitroxide **23** available, the substituent spin label would introduce spin density into the host semibullvalene ring system,³⁶ and coupling to the β -vinyl hydrogen would likely result. Should the semibullvalene nucleus be isomerizing rapidly on the esr time scale (*ca.* 10^7 sec⁻¹), this coupling would appear as a triplet. If isomerization were slow, doublets would be seen. Observation of a temperature dependence would permit a more accurate estimation of the isomerization rate than obtainable by pmr which can only set a lower limit because of its greater time scale.



Initial experiments with **21a** led without complication to **22a** in 45% yield. From the temperature-independent pmr behavior and the anticipated 1 (δ 4.93, t, $J = 3.5$ Hz):4 (3.92, m):2 (2.85, m) distribution of ring protons, it follows that **22a** is substituted at C₃.

Comparable hydrolysis of **21b** followed by air oxidation gave **22b** (57%) which proved to be the only crystalline semibullvalene encountered in this study. The infrared spectrum (KBr) shows a hydroxyl stretching mode at 3320 cm⁻¹. Also, the presence of a lone downfield triplet ($J = 4.0$ Hz) at δ 5.21, a four-proton multiplet centered at δ 4.14, and an upfield multiplet of area 2 at δ 3.01 is fully consistent with the 3-semibullvalenylcarbinol structure assignment.

Unfortunately, we have been singularly unsuccessful in all attempts to isolate aldehyde **22c**, the requisite precursor of **23**, from oxidation of **22b**. The broad spectrum of reagents examined have included dicyclohexylcarbodiimide and dimethyl sulfoxide,³⁷ ruthenium tetroxide in carbon tetrachloride,³⁸ pyridine-sulfur trioxide and triethylamine in dimethyl sulfoxide,³⁹ manganese dioxide,⁴⁰ and *N*-chlorosuccinimide-dimethyl sulfide with triethylamine.⁴¹ Our speculation in this matter centers about the extreme sensitivity of the desired carbonyl compound. This conclusion gains credibility from experiments conducted in particular with silver carbonate-Celite.⁴² When the progress of this oxidation was followed with time (pmr analysis), a singlet absorption was seen to appear at δ 9.76. However, storage of this solution at -30° under argon did not prevent diminution in the intensity of this signal. Along similar lines, complete decomposition was also noted during attempts to convert **21c** to 3-semibullvalenecarboxylic acid.

Discussion

The activation energy for degenerate structural isomerization in semibullvalene is sufficiently low³⁴ (estimated at 2.3⁴³-3.3 kcal/mol)⁴⁴ that speculation has recently cen-

tered around the possibility of realizing a "negative Cope transition state"^{20b,44,45} by proper substitution of this molecular framework. Both Hoffmann⁴⁵ and Dewar⁴⁴ have sought theoretical insight (EH and MINDO/2, respectively) into this question. The interesting deduction has been made that certain judiciously positioned substituents might well prove to stabilize or destabilize the bishomoaromatic six-electron transition state relative to the ground state. In the favorable cases, the suggestion has been advanced that mesovalent intermediates may very well become the actual stable forms.

Another interesting conclusion concerns the predicted effect of electron-donating and electron-withdrawing groups at C₁ and C₂. Given that the valence orbitals of semibullvalene contain the Walsh orbitals of cyclopropane or a set of comparable symmetry, then seemingly π -electron donors should shift the relevant equilibria markedly toward **14** and **19**, while π -electron acceptors will shift matters in the opposite direction.⁴⁵ Comparable rationalization had earlier been resorted to in explanation of the sensitivity of the norcaradiene-cycloheptatriene equilibrium to varying C₇ substitution.⁴⁶ However, at the outset of the present studies, there were no data to test the newer predictions.

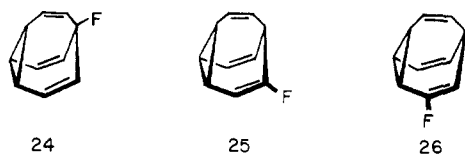
In addition to valence isomerizations in the norcaradiene-cycloheptatriene series,⁴⁷ rather sizable ground state equilibrium displacements had also previously been observed for variously substituted bicyclo[4.2.0]octadiene-cyclooctatriene pairs⁴⁸ and bullvalene derivatives.⁴⁹ However, these systems lack ideality owing to the heavily weighted thermodynamic preference for one of the constituent isomers. Two-fold degenerate systems do not possess this inherent structural disadvantage and consequently warrant detailed investigation of perturbational effects arising from framework substitution. In this connection, Schleyer has recently examined a limited number of barbaralones and has observed that deuterium exhibits a preference for bonding to aliphatic > cyclopropyl > olefinic carbon, while an inverse ordering prevails for methyl attachment: olefinic > cyclopropyl > aliphatic.⁵⁰

Our data with **13a** \rightleftharpoons **14a** and **19a** \rightleftharpoons **20a** compare favorably with the methylbarbaralone findings, evidently because similar influences are at work. In fact, the semibullvalene-derived equilibrium results clearly demonstrate decided preferential attachment to olefinic > cyclopropyl > aliphatic irrespective of the particular substituent. As regards the methyl group, its interaction with the semibullvalene ring can be expected to be donor dominant, the effect being achieved either by net electron donation or by polarization of the divinylcyclopropane system.⁵¹ Cyclopropane rings are known to enjoy π conjugative properties simulating those of π bonds. But in monosubstituted examples, specific bond weakening and strengthening effects on the *adjacent* and *remote* cyclopropane ring bonds require consideration as well. In this connection, the available experimental data denote that the bonding of a methyl group to a cyclopropane ring leads to a lengthening of the adjoining ring bond and a shortening of the remote C-C link.⁵² The π -acceptor substituents -CH₂⁺ (as in norcaradienylcarbinyliations)⁵³ and -CN⁵⁴ exert an influence comparable in direction although understandably of a higher order. In the **13a** \rightleftharpoons **14a** example, the dominance by **13a** at equilibrium conforms to this line of reasoning, although it is rather unlikely that this particular facet of the alkyl substituent effect is the sole contributing feature (note, for example, persistence of equilibrium in favor of the substituted cyclopropane form **13** when R is -CH₂OCH₃ and -CH₂OH). Ground state preference for methyl attachment to olefinic carbon in the **19a** \rightleftharpoons **20a** case agrees in principle with adjacent bond weakening effects but is probably controlled to a

higher level by the usual strong preference of methyl for attachment to sp^2 -hybridized carbon.^{49,55,56}

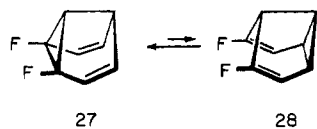
Given the reasonable assumption that the phenyl substituent in **13b** \rightleftharpoons **14b** can readily adopt a π interactive bisected conformation relative to the semibullvalene ring, the expectation follows that strengthening of the C_2C_8 σ bond will result,⁴⁵ and stabilization of isomer **13b** should ensue. Our data denote considerable equilibrium displacement in favor of **13b** such that it is essentially totally dominant at low temperatures. Accordingly, full agreement with theoretical prediction prevails.

As concerns fluorine substitution of fluxional molecules, Oth and Schröder have determined from pmr data that fluorobullvalene exists approximately 80–85% as isomer **24** where the electronegative group is bonded to the lone aliphatic carbon. The remainder of the mixture consists of **25** and **26**; no evidence for fluorine attachment to one of the three equivalent cyclopropyl sites was found. Nor is rotation out of conjugation possible, since the low-lying lone pair fluorine electrons are symmetrically disposed relative to the C–F bond. The resultant state of affairs is a decided preference for the ordering: aliphatic > olefinic > cyclopropyl.



This preference of fluorine for an aliphatic rather than cyclopropyl position has likewise been predicted from a theoretical analysis of the 1(5)-fluorosemibullvalene molecule.⁴⁵ Unfortunately, the present methods of synthesis¹² preclude access to this isomer, and the purported instability of **13-F** relative to **14-F** remains to be tested experimentally. Noteworthy, no such shifting of the **13** to **14** equilibrium to the right was uncovered in the somewhat limited series examined here.

The energetics associated with 2(4)-fluorosemibullvalene (**19c** \rightleftharpoons **20c**) are less obvious. In addition to the above, recent studies of 1,1-difluorocyclopropanes have shown this substitution pattern to exert an effect opposite to that of methyl, cyano, and the like with the remote ring bond experiencing significant weakening and the more proximate C–C link enjoying enhanced bonding characteristics.⁵⁸ Hoffmann's conclusions surrounding preferential existence of **14-F** conform to this general trend.⁴⁵ However, application of this model to **19c** \rightleftharpoons **20c** leads to the expectation that C_4C_6 bonding might be appreciable, but it seemingly is not. As with fluorosemibullvalene, preferential positioning of the halogen at an olefinic rather than cyclopropyl site is encountered. This result is also contrary to the predicted⁴⁵ strong equilibrium preference of 2,8-difluorosemibullvalene for structure **27** rather than **28**. Despite appreciable varia-



tions in substituent electronic properties and (assumedly) variations in bond order, the **19** to **20** equilibrium is shifted unidirectionally to the left. Extraction of those additional substituent effects which are making substantial impact must await the application of sophisticated theoretical analysis to such problems. Fortunately, such are beginning to make their appearance.⁵¹

We conclude by cautioning that our ignorance of the precise energetic realities operating in semibullvalenes warrants bridled extrapolation of the present data to other sys-

tems, particularly if grossly different structural features are involved.

Experimental Section

Infrared spectra were recorded with a Perkin-Elmer Model 467 spectrometer. The pmr spectra were obtained with Varian A-60A and HA-100 instruments, and apparent splittings have been cited in all cases. Mass spectra were measured with an AEI MS-9 mass spectrometer at an ionizing energy of 70 eV. Microanalyses were not acquired for the various semibullvalenes owing to their air sensitivity and thermal instability at room temperature.

Semibullvalene (8). **A. Method of Air Oxidation.** A stream of oxygen-free⁵⁹ nitrogen was bubbled for 15–30 min into a mixture of 5.0 g (17.9 mmol) of **9**, 7.0 g of potassium hydroxide, 45 ml of ethylene glycol, and 45 ml of water contained in a Claisen distilling flask. With continued nitrogen purging, the flask was heated strongly over a wire gauze and a Bunsen burner flame. Continued heating for 20–30 min resulted in the formation of a pale yellow distillate (50 ml). The distillate was diluted with water (50 ml) and extracted with hexane (3×50 ml). To the distilling flask was added 75 ml of water, and this solution was extracted thoroughly with ether (5×50 ml) and methylene chloride (2×50 ml). The combined organic layers were washed once with water, dried, and combined with the dried hexane solution. Evaporation at atmospheric pressure through an 8-in. Vigreux column gave a residue, distillation of which furnished 1.45 g (78%) of **8**, bp 40–45° (25 mm).

B. Manganese Dioxide Oxidation of Semicarbazide Intermediate. A 100-ml three-necked round bottom flask equipped with condenser, serum cap, magnetic stirrer, and stopper was charged with 500 mg (1.79 mmol) of **9** and 1.0 g (17.8 mmol) of potassium hydroxide. The flask was flushed with nitrogen, and 20 ml of isopropyl alcohol was introduced through the serum cap. The mixture was brought to reflux with stirring and held at this temperature for 45 min before cooling in ice. Hydrochloric acid (3 *N*) was added until pH \sim 2, and the mixture was stirred for 5 min. Ammonium hydroxide (3 *N*) was added dropwise to give pH \sim 8, at which point 6 ml of pentane and 1.56 g of manganese dioxide were introduced sequentially in single portions. The resulting black suspension was stirred for 1 hr at 0° and 30 min at room temperature. Decantation of the solution and rising of the remaining sticky solids with small amounts of pentane were followed by washing of the combined organic layers with water (2×50 ml) and brine (50 ml). The aqueous layers were reextracted with pentane, and the pentane layers were dried. Filtration gave a clear solution which when distilled as above gave a residue which was isolated by preparative vpc on a 6 ft \times 0.25 in. SF-96 on Chromosorb G column at 65°. There was isolated 85 mg (46%) of semibullvalene.

Cuprous Chloride Complex 11. A mixture of **9** (500 mg, 1.80 mmol), sodium hydroxide (300 mg, 7.5 mmol), and 2-propanol (30 ml) was refluxed for 1 hr under nitrogen, cooled in an ice bath, and brought to *ca.* pH 2 with 3 *N* hydrochloric acid. The remaining solid dissolved, and gas evolution was noted. After basification with 3 *N* ammonium hydroxide, the 2-propanol was removed *in vacuo*, and the resulting aqueous phase was partitioned between

Table I. Variable-Temperature Pmr Shift Data for **13a** \rightleftharpoons **14a** (δ , 60 MHz, TMS, CS_2 solution)

Temp, °C	Methyl	H ₂ ,H ₈	H ₃ ,H ₇	H ₄ ,H ₆	H ₅
+36	1.10 s	3.42 m	5.06 dd ^a	4.78 dd ^c	2.68 t ^d
-19	1.10 s	3.36 m	5.07 dd ^a	4.87 dd ^c	2.72 t
-26	1.10 s	3.34 m	5.07 dd ^a	4.87 dd ^c	2.72 t
-40	1.10 s	3.32 m	5.07 dd ^a	4.88 dd ^c	2.72 t
-46	1.10 s	3.31 m	5.07 dd ^a	4.90 dd ^c	2.73 t
-55	1.11 s	3.28 m	5.05 m ^b	4.91 m ^b	2.72 t
-65	1.11 s	3.27 m	5.07 m ^b	4.95 m ^b	2.74 t
-74	1.12 s	3.24 m	5.01 br m		2.74 t
-80	1.12 s	3.22 m	5.02 br m		2.75 t
-85	1.12 s	3.19 m	5.04 br m		2.75 t

^a $J_{3,4} = J_{6,7} = 4.0$; $J_{2,3} = J_{7,8} = 2.0$ Hz. ^b Partial overlapping of peaks. ^c $J_{3,4} = J_{6,7} = 4.0$; $J_{4,5} = J_{5,6} = 3.0$ Hz. ^d $J_{4,5} = J_{5,6} = 3.0$ Hz. All apparent splittings are rounded to the nearest 0.5 Hz.

Table II. Variable-Temperature Pmr Shift Data for **13b** \rightleftharpoons **14b** (δ , 100 MHz, TMS)

Temp, °C	Solvent	Phenyl	H ₂ ,H ₈	H ₃ ,H ₇	H ₄ ,H ₆	H ₅
+33	CD ₂ Cl ₂	7.10 m	3.43 m	5.21 m	5.43 m	3.31 t ^c
-58	CD ₂ Cl ₂	7.12 m	3.34 m	5.20 dd ^a	5.55 dd ^b	3.34 m
-68	CD ₂ Cl ₂ -Freon 11 (1:1)	7.10 m	3.31 br s	5.21 dd ^a	5.58 dd ^b	3.38 t ^c
-97	CD ₂ Cl ₂ -Freon 11 (1:1)	7.10 m	3.27 br s	5.20 dd ^a	5.60 dd ^b	3.39 t ^c
-113	CD ₂ Cl ₂ -Freon 11 (1:1)	7.10 m	3.25 br s	5.20 dd ^a	5.64 dd ^b	3.42 t ^c
-116	CD ₂ Cl ₂ -Freon 11 (1:1)	7.10 m	3.24 br s	5.21 dd ^a	5.64 dd ^b	3.43 t ^c
-126	CD ₂ Cl ₂ -Freon 11 (1:1)	7.10 m	3.22 br s	5.21 dd ^a	5.69 dd ^b	3.45 br s

^a $J_{3,4} = J_{6,7} = 5.0$; $J_{2,3} = J_{7,8} = 1.0$ Hz. ^b $J_{3,4} = J_{6,7} = 5.0$ Hz; $J_{4,5} = J_{5,6} = 2.5$ Hz. ^c $J_{3,4} = J_{5,6} = 2.5$ Hz. All apparent splittings are rounded to the nearest 0.5 Hz.

Table III. Variable-Temperature Pmr Shift Data for **13c** \rightleftharpoons **14c** (δ , 60 MHz, TMS)

Temp, °C	Solvent	Methyl	-OCH ₂ -	H ₂ ,H ₈	H ₃ ,H ₇	H ₄ ,H ₆	H ₅
+35	CD ₂ Cl ₂	3.20 s	3.35 s	3.37 m	5.12 m	5.12 m	3.04 t ^a
-41	CD ₂ Cl ₂ -Freon 11 (1:1)	3.24 s	3.35 s	3.23 m	5.14 m	5.26 m	3.08 t ^a
-69	CD ₂ Cl ₂ -Freon 11 (1:1)	3.24 s	3.35 s	3.18 m	5.14 m	5.30 m	3.09 t ^a
-107	CD ₂ Cl ₂ -Freon 11 (1:1)	3.27 s	3.36 s	3.14 m ^b	5.16 m	5.42 m	3.14 m ^b
-119	CD ₂ Cl ₂ -Freon 11 (1:1)	3.26 s	3.35 s	3.10 m ^b	5.16 m	5.45 m	3.10 m ^b

^a $J_{4,5} = J_{5,6} = 2.5$ Hz. ^b The signals due to H₂,H₈ and H₅ overlap substantially at these temperatures.

Table IV. Variable-Temperature Pmr Shift Data for **19a** \rightleftharpoons **20a** (δ , 60 MHz, TMS)

Temp, °C	Solvent	Methyl	H ₁	H ₂ ,H ₈	H ₅	H ₆	H ₇	H ₃
+42	CS ₂	1.78 d ^a	←-----	2.93 m	-----→	5.19 m	-----→	4.84 m
-21	CS ₂	1.82 d ^a	←-----	2.87 m	-----→	5.28 m	-----→	4.84 m
-39	CS ₂	1.81 d ^a	2.83 m	2.77 m	3.03 m	5.32 dd ^c	5.26 dd ^d	4.83 m
-57	CS ₂	1.82 d ^a	2.84 m	2.72 m	3.03 dd ^b	5.37 dd ^c	5.25 dd ^d	4.82 m
-76	CS ₂	1.82 d ^a	2.84 m	2.68 m	3.04 dd ^b	5.42 dd ^c	5.26 dd ^d	4.82 m
-101	CS ₂	1.83 d ^a	2.83 m	2.61 m	3.06 dd ^b	5.48 dd ^c	5.25 dd ^d	4.82 m

^a $J = 1.5$ Hz. ^b $J_{1,5} = 6.0$; $J_{3,6} = 2.0$ Hz. ^c $J_{6,7} = 5.0$; $J_{3,6} = 2.0$ Hz. ^d $J_{6,7} = 5.0$; $J_{7,8} = 1.5$ Hz. All apparent splittings are rounded to the nearest 0.5 Hz.

water (50 ml) and chloroform (25 ml). Swirling was necessary to dissolve some solid which had become deposited. The organic phase was dried, filtered, and evaporated to give a yellowish solid which was taken up in methanol (5 ml) and treated dropwise with a solution of 360 mg of cupric chloride dihydrate (2.11 mmol) in water until no additional complex formed (approximately 65% of the solution was added). Suction filtration and air drying of the brick-red solid afforded 56 mg (13.5%) of **11**, mp 94–95° dec (lit.¹⁸ mp 95–96° dec), which proved to be insoluble in water and the common organic solvents.

Decomposition of this complex (29 mg, 0.125 mmol) with 3 *N* aqueous ammonia in ether (2 ml) proved vigorous. The ether phase was dried and the product isolated by preparative vpc. There was isolated 4 mg (31%) of semibullvalene (identified by ir and pmr with the original sample).

1(5)-Methylsemibullvalene (13a \rightleftharpoons 14a). A mixture of 250 mg (0.85 mmol) of **12a**,¹² 477 mg (8.5 mmol) of potassium hydroxide, and 13 ml of isopropyl alcohol was refluxed under nitrogen with magnetic stirring at a bath temperature of 90° for 45 min. This solution was cooled in ice, acidified with 3 *N* hydrochloric acid, basified with 3 *N* ammonium hydroxide, and treated with pentane (6 ml) and manganese dioxide (750 mg) as described above. The analogous work-up furnished an intensely odoriferous orange oil which was purified by preparative vpc on a 2 ft \times 0.25 in. OV-11 column at 45° to give 49.8 mg (49%) of **13a** \rightleftharpoons **14a**. Calcd for C₉H₁₀: *m/e* 118.0782, found 118.0781 (see Table I).

1(5)-Phenylsemibullvalene (13b \rightleftharpoons 14b). A solution of 500 mg (1.71 mmol) of **12b**¹² and 1.0 g (17.8 mmol) of potassium hydroxide in 25 ml of 2-propanol was heated under reflux in the absence of oxygen for 30 min, cooled in ice, and treated with 3 *N* hydrochloric acid to render the mixture acidic. After stirring for 5 min at 0°, the mixture was basified with 3 *N* ammonium hydroxide solution, 10 ml of pentane and 1.50 g of manganese dioxide were added, and stirring was continued for 30 min at room temperature (cessation of nitrogen evolution). The black suspension was vacuum filtered, the filtrate added to 100 ml of water, and the aqueous mixture extracted with pentane (2 \times 100 ml). The dried organic layers were concentrated to small volume, and the concentrate was

subjected to preparative vpc separation on a 1 ft \times 0.25 in. OV-11 column at 100°. There was obtained 232 mg (76%) of **13b** \rightleftharpoons **14b** as a colorless oil: ν_{\max} (neat) 3030, 2950, 1610, 1575, 745, and 697 cm⁻¹. Calculated for C₁₄H₁₂: *m/e* 180.0939, found 180.0943 (see Table II).

1(5)-Methoxymethylsemibullvalene (13c \rightleftharpoons 14c). In an analogous manner, diazasnoutane **12c**¹² (250 mg, 1.24 mmol) was partially hydrolyzed with 250 mg (6.2 mmol) of sodium hydroxide in 15 ml of 2-propanol. Subsequent oxidation with manganese dioxide (2.0 g) and preparative vpc purification on a 6 ft \times 0.25 in. 5% SE 30–3% KOH column at 80° yielded 72 mg (39%) of **13c** \rightleftharpoons **14c**. Calcd for C₁₀H₁₂O: *m/e* 148.0888, found 148.0890 (see Table III).

1(5)-Semibullvalenylcarbinol (13d \rightleftharpoons 14d). A mixture of 300 mg (0.85 mmol) of **12d**-OAc,¹² 150 mg (3.75 mmol) of sodium hydroxide, and 15 ml of 2-propanol was brought to reflux under nitrogen while being stirred magnetically. After 2 hr, the solution was cooled in ice, and 3 *N* hydrochloric acid was added. Decarboxylation occurred as the pH was adjusted to 2. Aqueous ammonia (3 *N*) was introduced to return the pH to ca. 8, and this mixture was added to 100 ml of water and extracted with methylene chloride (6 \times 10 ml). The combined organic layers were washed with water, 0.3 *N* hydrochloric acid, saturated sodium bicarbonate solution, and brine. Drying and solvent evaporation was followed by preparative tlc on silica gel (elution with 20% ether in carbon tetrachloride) to give 62 mg (54%) of the carbinol as a pale yellow oil: δ_{TMS} (CCl₄) 4.87–5.22 (m, 4), 3.50 (s), overlapping 3.42–3.60 (m, 4 total), 3.27 (s, 1, -OH), and 3.02 (t, $J = 3.0$ Hz, 1). Calcd for C₉H₁₀O: *m/e* 134.0732, found 134.0733.

2(4)-Methylsemibullvalene (19a \rightleftharpoons 20a). Hydrolysis-oxidation of **18a**¹² (250 mg, 0.85 mmol) following exactly the procedure described for **12a** afforded after preparative vpc under comparable conditions 53 mg (52%) of **19a** \rightleftharpoons **20a** as a colorless liquid. Calcd for C₉H₁₀: *m/e* 118.0782, found 118.0781 (see Table IV).

2(4)-Methoxymethylsemibullvalene (19b \rightleftharpoons 20b). In a similar manner, diazasnoutane **18b**¹² (517 mg, 1.60 mmol) was partially hydrolyzed with 320 mg (8 mmol) of sodium hydroxide in 20 ml of 2-propanol. Subsequent oxidation with manganese dioxide (2.0 g) and preparative vpc purification on the SE-30/KOH column yield-

Table V. Variable-Temperature Pmr Shift Data for **19b** \rightleftharpoons **20b** (δ , 60 MHz, TMS)

Temp, °C	Solvent	Methyl	-OCH ₂ -	H ₇	H ₃	H ₆	H ₈	H ₂	H ₁ , H ₅
+60	CDCl ₃	3.33 s	3.94 AB ^a	5.22 dd ^b	5.16 br d ^c	4.71 m	3.76 m	3.72 m	3.11 m 3.06 m
+30	CDCl ₃	3.34 s	3.94 AB ^a	5.28 dd ^b	5.12 br d ^c	4.73 m	3.76 m	3.72 m	3.13 m 3.07 m
-1	CDCl ₃	3.35 s	3.95 AB ^a	5.29 dd ^b	5.14 br d ^c	4.74 m	3.77 m	3.73 m	3.16 m 3.08 m
-32	CDCl ₃	3.37 s	3.96 AB ^a	5.32 dd ^b	5.22 br d ^c	4.73 m	3.82 m	3.78 m	3.18 m 3.11 m
-42	CD ₂ Cl ₂ -Freon 11 (1:1)	3.31 s	3.91 AB ^a	5.27 dd ^b	5.14 br d ^c	4.77 m	3.67 m	3.62 m	3.14 m 3.05 m
-81	CD ₂ Cl ₂ -Freon 11 (1:1)	3.32 s	3.93 AB ^a	5.29 dd ^b	5.16 br d ^c	4.79 m	3.69 m	3.64 m	3.17 m 3.07 m
-101	CD ₂ Cl ₂ -Freon 11 (1:1)	3.34 s	3.93 AB ^a	5.30 dd ^b	5.18 br d ^c	4.79 m	3.71 m	3.69 m	3.19 m 3.08 m

^a $J_{AB} = 11.5$ Hz with downfield portion further split by H₃ ($J = 1.0$ Hz). ^b $J_{7,8} = 4.0$; $J_{6,7} = 3.0$ Hz. ^c $J_{2,3} = 3.0$ Hz. All apparent splittings are rounded to the nearest 0.5 Hz.

Table VI. Variable-Temperature Pmr Shift Data for **19c** \rightleftharpoons **20c** (δ , 60 MHz, TMS)

Temp, °C	Solvent	H ₁ , H ₂ , H ₃	H ₅	H ₃	H ₆	H ₇
+35	CS ₂	2.84 br m	3.17 m	4.62 m		5.41 m
+13	CS ₂	2.83 br m	3.18 m	4.62 m		5.43 m
-8	CS ₂	2.79 br m	3.18 dd ^a	4.59 dd ^b		5.45 m
-31	CS ₂	2.75 br m	3.18 dd ^a	4.59 dd ^b	5.53 dd ^c	5.43 dd ^d
-53	CS ₂	2.72 br m	3.19 dd ^a	4.58 dd ^b	5.58 dd ^c	5.42 dd ^d
-64	CS ₂	2.68 br m	3.18 dd ^a	4.57 dd ^b	5.59 dd ^c	5.42 dd ^d
-70	CS ₂	2.68 br m	3.19 dd ^a	4.58 dd ^b	5.61 dd ^c	5.43 dd ^d
-80	CS ₂	2.67 br m	3.18 dd ^a	4.57 dd ^b	5.63 dd ^c	5.41 dd ^d
-91	CS ₂	2.66 br m	3.18 dd ^a	4.57 dd ^b	5.65 m	5.43 dd ^d

^a $J_{1,2} = 4.0$; $J_{3,6} = 2.0$ Hz. ^b $J_{3,4} = 2.5$; $J_{2,3} = 1.5$ Hz. ^c $J_{6,7} = 5.0$; $J_{3,6} = 2.0$ Hz. ^d $J_{6,7} = 5.0$; $J_{7,8} = 2.5$ Hz. All apparent splittings are rounded to the nearest 0.5 Hz.

ed 99 mg (42%) of **19b** \rightleftharpoons **20b**. Calcd for C₁₀H₁₂O: m/e 148.0888, found 148.0890 (see Table V).

2(4)-Fluorosemibullvalene (19c \rightleftharpoons **20c**). A mixture of 250 mg (0.84 mmol) of **18c**¹² and 473 mg (8.43 mmol) of potassium hydroxide in 13 ml of 2-propanol was heated at reflux under nitrogen with magnetic stirring for 45 min. Subsequent acidification, basification, and manganese dioxide (750 mg) oxidation in the predescribed manner gave a colorless solution which was concentrated to a volume of 2 ml by careful removal of the pentane by distillation through a 6-in. Vigreux column. Vpc fractionation of the residual liquid on the 2-ft OV-11 column at 45° afforded 73.4 mg (71.5%) of pure **19c** \rightleftharpoons **20c**. Calcd for C₈H₇F: m/e 122.0532, found 122.0530 (see Table VI).

3-Methoxymethylsemibullvalene (22a). Treatment of 300 mg (0.93 mmol) of **21a**¹² with 200 mg (5.0 mmol) of sodium hydroxide in 10 ml of 2-propanol at reflux under nitrogen for 1.5 hr and subsequent processing and oxidation (2.0 g of manganese dioxide) as before gave after vpc isolation on the SE-30/KOH column 62 mg (45%) of **22a** as a clear, colorless liquid: δ_{TMS} (CCl₄) 4.93 (t, $J = 3.5$ Hz, 1), 3.92 (m, 4), 3.55 (s, 2), 2.98 (s, 3), and 2.85 (m, 2) (temperature invariant). Calcd for C₁₀H₁₂O: m/e 148.0888, found 148.0890.

3-Semibullvalenylcarbinol (22b). A mixture of 200 mg (0.57 mmol) of **21b**¹², 150 mg (3.85 mmol) of sodium hydroxide, and 10 ml of 2-propanol was refluxed under nitrogen for 1 hr. The cloudy reaction mixture was cooled in ice, while 3 *N* hydrochloric acid was added to bring the pH to ca. 2. The solid that was present dissolved, and the solution became purple in color. After being stirred for 5 min, this solution was returned to pH 8 with 3 *N* ammonium hydroxide, treated with 300 ml of water, and extracted with chloroform (6 \times 15 ml). The combined organic layers were washed with water and brine, dried, and evaporated *in vacuo*. The resulting oil was chromatographed on a short Florisil column (1.5 \times 10 cm). Elution with ether-pentane (1:1) gave a white solid, recrystallization of which from pentane-ether furnished 43 mg (57%) of **22b** as white needles, mp 71–71.5°: ν_{max} (KBr) 3320, 1350, 1007, 819, 759, 731, and 703 cm⁻¹; δ_{TMS} (CDCl₃) 5.21 (t, $J = 4.0$ Hz, 1), 4.14 (m, 4), and 4.01 (s, 2) (temperature invariant). Calcd for C₉H₁₀O: m/e 134.0732, found 134.0733.

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