Isomerization Behavior of 2,8-Tetramethylenesemibullvalene under Thermal, Photochemical, and Metal Catalyzed Conditions. An Excited State Semibullvalene–Semibullvalene Rearrangement

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Abstract: Evidence is presented that 2,8-tetramethylenesemibullvalene can partake of at least four distinct types of isomerization reactions under differing conditions. Upon thermal activation, this hydrocarbon is rearranged exclusively to 1,2-tetramethylenecyclooctatetraene, an interconversion which requires the 1,3 alkyl chain to undergo concurrent translocation with the C_8 framework. In contrast, triplet sensitized (acetone) irradiation gives rise to an isomeric annulated semibullvalene in which the bracketing alkyl chain is now 1,2 disposed. This remarkable rearrangement, which is seemingly triggered by initial di-π-methane bonding, is the first example of a semibullvalene to semibullvalene interconversion under any conditions. The title hydrocarbon rearranges also in the presence of alumina, "magnesium bromide," and rhodium dicarbonyl chloride dimer with formation of a ring opened triene lacking the cyclopropane ring; deprotonation of one of the methylene groups bonded directly to the semibullvalene framework also occurs. Subjection of 2,8-tetramethylenesemibullvalene to the action of anhydrous silver perchlorate in benzene at room temperature does not result in comparable isomerization but gives rise instead solely to an annulated bicyclo[3.2.1]octatriene. To gain additional mechanistic insight into each of the four rearrangements, recourse was made to deuterium labeling experiments. On the basis of such data, reasonable mechanisms are advanced in explanation of the varied isomerization pathways.

The special geometry of semibullvalene, reknown for its ability to markedly enhance the rate of degenerate Cope rearrangement (lifetime of an isomer is less than 3×10^{-7} sec at 0°), has provoked investigation of varied synthetic approaches to the hydrocarbon,[2] detailed structural (electron diffraction)[3] and orbital sequencing (PE) studies,[4] low temperature pmr measurements,[2d,m,n,5a–c,g] and theoretical assessment of its possible neutral homoaromatic character.[5e,f] However, the potentially intriguing chemical consequences of such a continuous cyclic array of six peripheral $\sigma\pi$ interacting electrons have not yet received the full attention they merit. Recent reports have called attention to semibullvalene's remarkable capacity for reaction with transition metal complexes leading to organometallic structures of various types.[6] Its stereoselective 1,4 bromination,[7] susceptibility to acid-catalyzed addition of protic solvents,[8] and capacity for photochemical[2g] and thermal isomerization[9] to cyclooctatetraene are also matters of record. We recently uncovered a route to the first examples of 2,8-annulated semibullvalenes[5b,c,10] and have undertaken to examine the propensity of a prototypical member of this series for structural isomerization. In this paper, we focus attention in particular upon rearrangements of the 2,8-tetramethylene derivative under conditions of thermal and photochemical activation, as well as on varied bond reorganizations arising from interaction with several metal catalysts.

Thermochemical Behavior. Earlier work from this laboratory demonstrated that cyclooctatetraene is formed as the sole product of the gas phase thermolysis of semibullvalene at 400° (30 mm; contact times of 1–3 sec).[9b] Interest in this reaction was heightened by the awareness that it proceeds unidirectionally and therefore qualifies as the preferred method for the directed synthesis of certain disubstituted cyclooctatetraenes.[9a] The high yield isomerizations of 1 and 3 illustrate not only the positional selectivity of the process but also provide the suggestion that rearrangement probably proceeds by a two-step bond cleavage process involving bicyclo[3.3.0]octadienediyl intermediates.
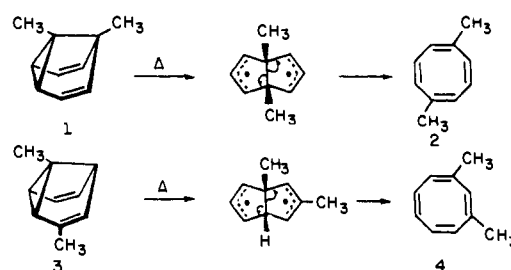

Strict adherence by the title hydrocarbon 5 to rearrangement by this mechanism would lead to the severely strained 1,3-tetramethylenecyclooctatetraene molecule. It was therefore of interest to examine the consequence of such steric strain on the course of the thermally promoted bond reorganization. In gas-phase experiments conducted at 460–500° (1.5 mm), 5 did afford a cyclooctatetraene product in 69% yield. This material was identified, however, as the known 1,2-tetramethylene derivative[10,11] on the basis of its characteristic infrared and pmr absorptions and conversion to the TCNE adduct of established structure. The isolation of this particular product necessitates that the 1,3-tetramethylene chain in 5 undergo concurrent translocation in a fashion which eventuates in its vicinal attachment to the medium ring in 6.
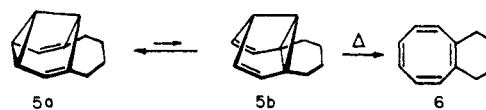
Having observed this somewhat unusual rearrangement, we were led to gain further insight into its mechanism. For this purpose, the 1,5-dideuterio derivative 11 was prepared. As outlined in Scheme I, Diels–Alder addition of N-phenyltriazolinedione to available 11,12-dideuterio[4.4.2]propella-2,4,11-triene (7),[11] followed by acetone-sensitized photocyclization to give 9, Ag$^+$-catalyzed rearrangement to generate 10, and ultimate hydrolysis-oxidation proceeded

in entirely precedented fashion[5c,9] to give the isotopically labeled hydrocarbon. In this instance, thermal isomerization was conducted at somewhat lower temperatures (460° (1.5 mm); contact time *ca.* 1 sec) than those originally employed for two reasons. First, incomplete conversion of **11** to **12** occurs under these conditions, and consequently it is possible to recover semibullvalene and search for isotopic scrambling in the starting material. None was observed by pmr analysis. Secondly, these conditions are sufficiently subdued that deuterium migration likewise does not operate in the annulated cyclooctatetraene product **12**.[12] The samples of 1,2-tetramethylenecyclooctatetraene-d_2 obtained from pyrolysis of **11** were separated from the semibullvalene by preparative vpc and converted individually to their TCNE adducts. Specific location of the deuterium atoms directly in **12** is not readily achievable by pmr techniques, because its olefinic protons appear as closely spaced multiplets at both 60 and 100 MHz. The selection of TCNE as dienophile was predicated on the fact that it reacts exclusively under mild conditions with that valence isomer of **6** having the cycloalkane ring fused to the cyclobutene moiety. The pmr spectra of the adducts revealed the absence of both an sp^3-bound proton in the cyclobutene ring and a hydrogen from the pair H$_7$,H$_8$. Thus, the problem became one of distinguishing between **13** and **14**. Resolution of this question was made possible by LAOCOON III computer simulation of the 100-MHz pmr spectra of these isomeric adducts.[13] The parameters employed were derived from the unlabeled tetranitrile and are as follows: $H_{2,5} = \delta$ 3.34, $H_{1,6} = 4.02$, $H_{7,8} = 6.485$; $J_{7,8} = 8.0$, $J_{1,8} = J_{6,7} = 6.6$, $J_{2,5} = 6.0$, $J_{1,2} = J_{5,6} = 3.5$, $J_{1,7} = J_{6,8} = 1.2$, $J_{1,6} = J_{2,8} = J_{5,7} = 0.5$ Hz. By this technique, we observed that the combined absorption due to H$_1$ and H$_6$ differs markedly in the two compounds, and that the spectra of the isolated product conform uniquely to that pattern computed for **13**. Consequently, the annulated cyclooctatetraene derived from thermal rearrangement of **11** is isotopically substituted predominantly, and perhaps exclusively, as in **12**.

Scheme I
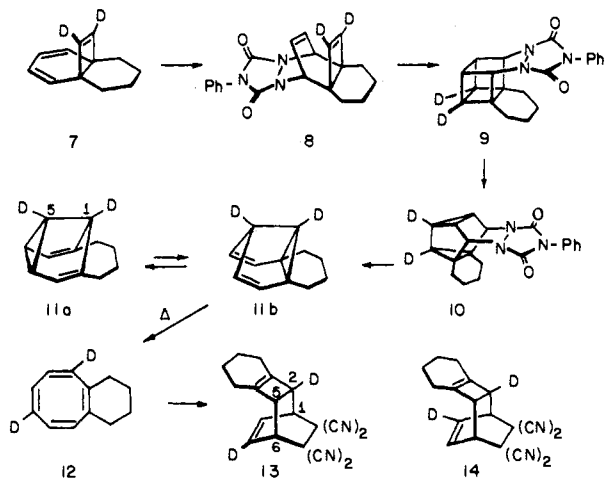
The 1,4-disposition of the deuterium atoms in **12** requires that C$_1$ in **11a** ⇌ **11b** ultimately becomes transposed with one of the adjacent bridgehead carbon atoms. One possible mechanism involves homolytic cleavage of a strained cyclopropyl bond in the only mode which can possibly give rise to two allylically stabilized radical centers. The ensuing intermediate **15** could then experience bond reorganization with formation of the 2,8-bridged bicyclo[4.2.0]octatriene (**17**) (Scheme II). This conversion could operate by way of a simple 1,2-alkyl shift in **15**[14] or less directly by homolytic

cleavage of the symmetrically disposed central σ bond to give 1,3-tetramethylenecyclooctatetraene (**16**) and its subsequent valence isomerization. Our data do not, of course, permit a possible distinction to be made between these two rationalizations. Suffice it to say that the findings are not incongruent with the initial formation of **16**, and the driving force for its conversion to **17** is fully anticipated from its excessive ground-state strain. Intramolecular Diels-Alder bonding in **17** to give bishomobenzene **18**, and ultimately **12**, parallels the intermediacy of such tetracyclo[4.2.0.0^{2,8}.-0^{5,7}]octenes in the pyrolytic conversion of bicyclo[4.2.0]octatrienes to cyclooctatetraenes[11] and in the thermal rearrangement reactions of cyclooctatetraenes.[12]

Scheme II

* denotes deuterium
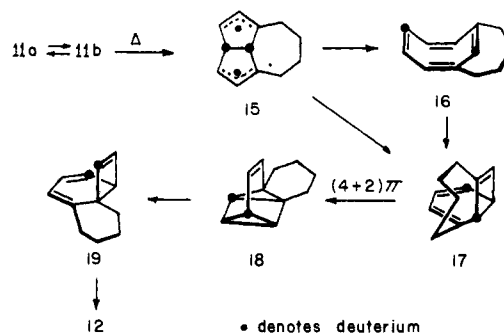
Photoisomerization. Zimmerman and coworkers[2d,g] have determined that semibullvalene and 1,3,5,7-tetramethyl-semibullvalene (**20**) are capable of acetone-sensitized photorearrangement to cyclooctatetraene and **21**, respectively. From consideration of the alternating carbon substitution pattern in **21**, direct analogy with the thermal isomerization pathway (*vide supra*) is seen. This may be due to close approach of excited and ground states which facilitates intersystem crossing of electronically excited bicyclo[3.3.0]-octadienediyl biradicals to lower vibrational levels followed by ring opening. However, the limited number of examples studied to this time does not yet allow for sweeping mechanistic conclusions.
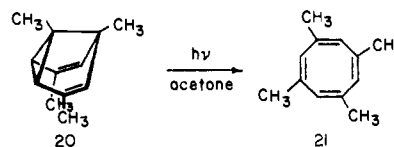

Owing to the structural restrictions inherent in **5** which lead directly to modification of the reactivity of **15**, perturbation of one or more of the photochemical steps can be anticipated if such an intermediate does in fact intervene. We therefore examined the excited state behavior of this annulated semibullvalene. No cyclooctatetraenes were produced; rather, the first example of an intriguing semibullvalene-semibullvalene rearrangement was encountered.

Direct irradiation of **5** in cyclohexane through quartz with 2537-Å incident light gave rise to a multitude of products, none of which was formed at a dominant concentration level. In contrast, when the triplet-sensitized irradiation of **5** was carried out in acetone solution at 3000 Å (Pyrex optics) and followed by intermittent vpc analysis, a single new substance made its appearance rather quickly. With increasing time, the peak associated with this product gradually decayed, and several new minor components were seen. Considerable polymer formation was also in evidence. For preparative scale work a bank of seven Pyrex test tubes, each containing 23.6 mg of **5** dissolved in degassed acetone, was irradiated for 2 hr in a Rayonet reactor equipped with a

"merry-go-round" device. Isolation from a 5% PMPE (five-ring) vpc column returned 40% of unreacted **5** and gave 6.2% of the new hydrocarbon. This air-sensitive compound was found to be isomeric with **5** by accurate mass measurement (parent ion at m/e 158.1098). Its ultraviolet spectrum consists of a shoulder at 235 nm (ϵ 3200) on the end of otherwise intense end absorption, the similarity of which to the electronic properties of **5** and other alkyl substituted semibullvalenes proving to be particularly striking.[2n,5c] The 100-MHz pmr spectrum in $CDCl_3$ at 35° shows a total of three olefinic protons, one appearing as a doublet at δ 5.6 (J = 6 Hz), the second as a doublet of doublets (J = 6 and 2 Hz) centered at δ 5.34, and the third as a broadened singlet at δ 4.9. In addition, three cyclopropyl protons are present, two of which are allylic (δ 2.86, d, J = 5 Hz) and the other more shielded (δ 2.60, t, $J \approx$ 6 Hz). Also, the tetramethylene chain is now positioned such that one methylene group is allylic (2.36, m, 2 H) by comparison to the other three (δ 1.2-1.9, m, 6 H). Double resonance studies showed the olefinic hydrogens not to be strongly coupled to the higher field protons but did give evidence of spin-spin interaction between the olefinic proton at δ 5.34 (collapse to a doublet with J = 6 Hz) and the cyclopropyl hydrogens at δ 2.86. Variable-temperature measurements from +35 to −92° witnessed major changes in the δ 5.6 (downfield shifting) and 2.86 (migration to higher field) doublets.

This temperature-dependent behavior likewise is fully compatible with a semibullvalene structural assignment. The presence of three rather than four olefinic protons and the unsymmetrical nature of the tetramethylene bridge serve to rule out **22** as the correct structure. Neither does it follow that **23** is the photoproduct. Isomer **23b** contains only

22   23a   23b

24a   24b
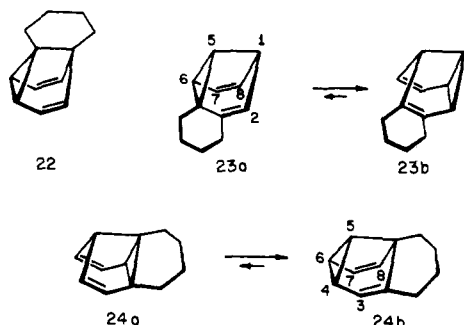
two olefinic hydrogens and is clearly incompatible with the data. Furthermore, not only is it implausible that **23a** be the dominant valence tautomer under ordinary conditions,[2m,n,5c] but should this be the case, several of the pmr features are in such complete discord with the structural hypothesis as to discredit it.[15] Rather, all data are entirely consistent with formulation **24** which, by virtue of its alkyl substitution, resides chiefly in form **24b**. Any question that the bridging be of some other type[16] is reasonably removed upon comparison of the low field segments of the pmr spectra (60 MHz) of the photoproduct and 2(4)-methylsemibullvalene, the near superimposability of which at the appropriate temperatures is indeed remarkable (Figure 1). This assignment of structure is further substantiated by the finding that H_6 (δ 2.86) spin interacts to the extent of 2 Hz with H_7 (5.34) and H_4 (2.86) at approximately the same level with H_3 (4.9). The increase in olefinic character at C_8 (δ 5.6) coupled with added cyclopropyl character at C_4 and C_6 (2.86) with decreasing temperature conforms plausibly with the gradual added concentration advantage expected for **24b** under these conditions.[2m,n,5c]

Interestingly, the photoisomerization of **5** again results in the permutation of a 1,3-bridged tetramethylene system to
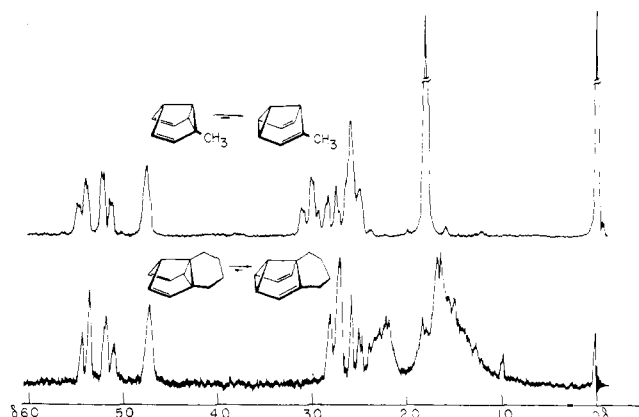
Figure 1. The 60-MHz pmr spectra of (top) 2(4)-methylsemibullvalene and (bottom) 1,2-tetramethylenesemibullvalene in CS_2 solution. The spectra were recorded at −101 and +35°, respectively, to equalize as much as possible the concentration gradients of the two valence isomers in the samples.

one that incorporates a 1,2-annulated framework. However, in this particular instance the novel and unprecedented conversion of one semibullvalene isomer to another has occurred. For the purpose of mechanistic deduction, recourse was again made to dideuterio derivative **11**, which for this particular series of experiments was labeled to the extent detailed in structure **25** (pmr analyses). The rearranged semibullvalene isolated from sensitized photoisomerization of **25** was subjected to quantitative pmr integration at 100 MHz and determined to be isotopically substituted as in **26**. Several significant points thereby emerge. Firstly, skeletal bond reorganization operates in a manner such as to preclude the entry of deuterium at position 3. Secondly, although a sizable fraction of the isotope attached to the original bridgehead sites in **25** turns up bonded to C_7 and C_8 in **26**, dilution does occur in a way that leads to a nearly equitable smaller influx of deuterium at C_4,C_5 and C_6. Since any combination which relates a methine group from the first set (53% D) to a methine of the second set (16-17% D) gives rise to a fractionation factor of at least 3.1, it becomes clear that a single intermediate cannot be involved, because the number is too large to originate from conventional secondary deuterium isotope effects. Recovered **25** appeared not to be isotopically scrambled (pmr analysis).


25   26
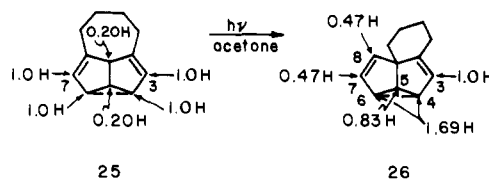
Two mechanisms seem especially reasonable, and these are outlined in Scheme III. Both are initiated by vinyl-vinyl bonding of the di-π-methane moiety in **11** with formation of "biradical" **27**.[17] Relocation of the odd electron density in this intermediate is capable of leading via **28** or **29** and then **30** to **32** in which the deuterium distribution is necessarily at C_7 and C_8. The predominance of isotopic labeling at these sites in the photoproduct supports the assumption that this pathway may be dominant. Alternatively, **28** and **29** can undergo cyclopropane ring opening with formation of barrelene **31**. The structural features of this triene are such that it can expectedly[2d] serve as the precursor to annulated semibullvalenes **32-34**. The inequality in the levels of isotopic substitution at C_4, C_6, and C_5 (cf. **26**) in the photoproduct is considered to perhaps arise from a fortuitous combination of experimental error, isotope effects, and/or some-

what less than fully equitable deuterium labeling in the two bridgehead positions of the starting material.

Scheme III
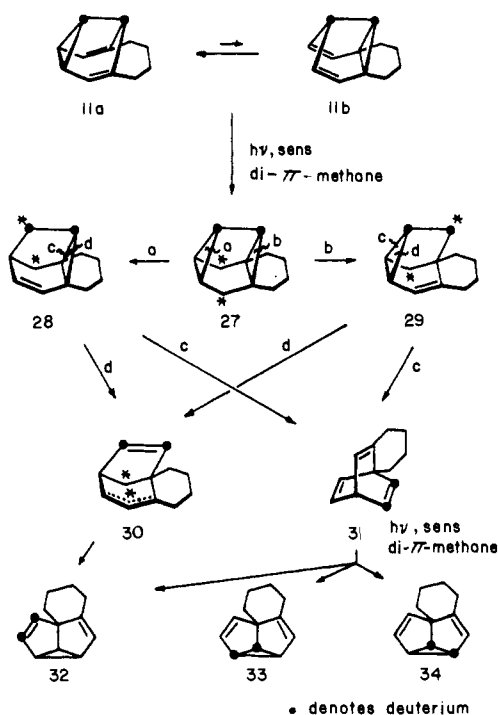
In attempts to independently establish the photolability of **31**, a rather exhaustive, although ultimately unsuccessful study of its preparation in unlabeled form was undertaken. We have found, for example, that the α-pyrone, 5,6,7,8-tetrahydrocoumarin (**35**),[18] is capable of double Diels-Alder reaction with such dienophiles as maleic anhydride,[18,19] ethyl acrylate, and methyl vinyl ketone with formation of adducts **36**, **37a**, and **37b**, respectively. However, intensive investigation of established[20] and new methods for conversion of these different types of side chain to internal double bonds were uniformly unrewarding. Attempts to interrupt the photoisomerization of **5** in its very early stages also did not serve to provide indication of the barrelene.
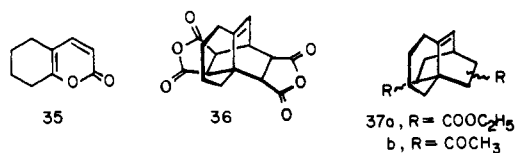

Despite the unavailability of **31** (as the d_0 or d_2 species), sufficient precedent is now available in the form of aromatic fused barrelenes[21] as well as the parent hydrocarbon[2d] to be of the conviction that this bridged triene will also be especially prone to excited state di-π-methane rearrangement.

The Rearrangement Promoted by Alumina, Magnesium Bromide, and Rhodium Dicarbonyl Chloride Dimer. The recent recognition that strained molecules are subject to rearrangement when treated under very mild conditions with various metal catalysts has played an important role in broadening our understanding of the reactivity of these systems.[22] As a continuation of our interest in such processes, an examination of the susceptibility of **5** for metal-catalyzed isomerization was undertaken. Immediate discovery was made that treatment of the semibullvalene with mercuric bromide in ether[23] produced an intractable tarry residue. This suggested that utilization of a less powerful cata-

lyst was in order. Subsequent studies involving the use of slurried activity I alumina (neutral or basic) in pentane revealed a capacity of **5** for rapid and quantitative conversion to a single new substance under these conditions. Subsequently, chromatographic elution of **5**, through a column of alumina supplanted the earlier method as the procedure of choice for preparative scale work.

The product was a colorless oil whose temperature-independent pmr shows the presence of four olefinic protons at δ 5.95 (s, 2), 5.67 (m, 1), and 5.15 (m, 1), two protons of intermediate chemical shift (complex multiplet at δ 3.42-4.08), and eight more shielded hydrogens (broad manifold in the δ 1.0-2.9 region). The electronic spectrum in isooctane which consists of three maxima at 236 (ϵ 14,000), 243 (14,000), and 262 sh nm (5600) serves to establish the presence of a heteroannular 1,3 diene unit.[24] The isomeric nature of the hydrocarbon was established by elemental analysis and mass spectral molecular weight determination.

The inability of the rearrangement product to react with N-phenyltriazolinedione suggested that the chromophore was a rigid s-trans diene, and the possibility was considered that the overall structure was **38**.[25] In confirmation of this assignment, catalytic hydrogenation of **38** over 5% rhodium on carbon in tetrahydrofuran-glacial acetic acid solution afforded the perhydro derivative **39** whose high resolution infrared and 100 MHz pmr spectra were superimposable upon those of the reduction product of **40** and **5**.[5c]
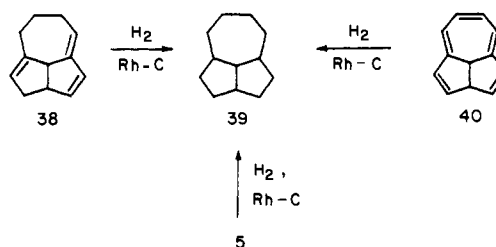
That the bond reorganization involved in the isomerization of **5** to **38** does not involve unexpected deep-seated bond migration became evident when **11** was subjected to the identical reaction conditions. A priori one would anticipate **41** to contain the indicated deuterium labeling pattern if a minimum number of bonds were being cleaved. The isotopically substituted product was seen to give a pmr spectrum similar to that of **38** except for the complete absence of the two proton multiplet at δ 3.42-4.08, simplification of the δ 5.67 signal to a triplet, and slight alteration of fine structure in the broad high field multiplet. Any possibility that the deuterium atoms are positioned elsewhere than at the bridgehead sites is not supported by the spectral data.
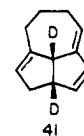

Although alumina is most efficient in effecting this isomerization, magnesium bromide and rhodium dicarbonyl chloride dimer were also found to promote the identical structural change. Thus, an ethereal solution of anhydrous $MgBr_2$, prepared by reaction of "reagent grade" magnesium with 1,2-dibromoethane, effected complete conversion of **5** to **38** after 15 min at room temperature. However, substitution of triply sublimed magnesium for the somewhat less pure metal led to a total inability to effect rearrangement. A minor metal contaminant, such as iron, copper, and the like which is present in the "reagent grade" material, is therefore presumed responsible for promoting the

isomerization. Although this point was not exhaustively examined, the finding did suggest that transition metals should be particularly effective. Indeed, when 5 was treated with a catalytic quantity of rhodium dicarbonyl chloride dimer in chloroform, the identical rearrangement was evidenced. But because concomitant decomposition of the semibullvalene also operates under these conditions, this method is not recommended for the preparation of 38.

Speculation of a mechanistically plausible path for this isomerization centers about initial oxidative addition of the metal atom into the peripheral cyclopropyl bond of the predominant valence isomer (5a)[6c] or directed electrophilic attack at C_4 or C_6 (Scheme IV). One hypothetical route leads directly to 43, while the other requires subsequent heterolytic opening of that strained four-membered ring which contains the metal. A feasible conversion of 43 to product triene is illustrated without belaboring the details.

Scheme IV

• denotes deuterium
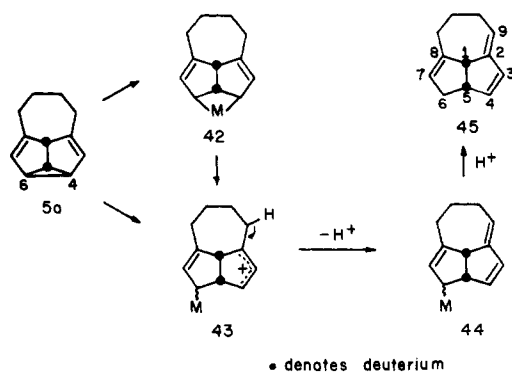
In ancillary studies, we have noted that benzosemibullvalene and 1,5-dimethylsemibullvalene are not prone to rearrangement with the above catalyst systems. On the other hand, annulated hydrocarbon 5 also undergoes the predescribed structural change when treated with anhydrous p-toluenesulfonic acid in dry benzene. A second product is now simultaneously formed in 10% relative yield, the structure of which proved to be identical with that of the compound formed exclusively upon silver-catalyzed rearrangement (*vide infra*). p-Toluenesulfonic acid is seemingly unique in the sense that it represents the only reagent studied which was found capable of partitioning 5 simultaneously along two rearrangement channels.

Ag+-Catalyzed Isomerization. The unique ability of Ag^+ to promote unparalleled rearrangement of bicyclo[1.1.0]butanes[26] and cubyl systems[27] has been amply demonstrated.[28] Its intrinsic electronic properties induce structural perturbations which are not frequently matched by other catalysts. This general characteristic of Ag^+ is again demonstrated herein as witnessed by the reaction of 5 with catalytic amounts of anhydrous silver perchlorate in dry benzene. After 30 min at room temperature, a single new isomeric compound was produced. The colorless oil (in isooctane) displays an intense ultraviolet maximum at 243 nm (ϵ 12,000) revealing thereby the presence of a heteroannular 1,3-diene system. Noteworthy pmr features are the five olefinic protons seen as a trio of multiplets at δ 5.85–6.20 (2 H), 5.60–5.84 (2 H), and 5.44–5.60 (1 H), one doubly allylic hydrogen (δ 2.75–3.05, m), and a pair of allylic protons (δ 2.05–2.45, m). The hydrocarbon was unreactive toward N-phenyltriazolinedione, tetracyanoethylene, and rhodium dicarbonyl acetonylacetonate. Epoxidation with m-chloroperbenzoic acid at 0° gave three thermally labile epoxides which defied characterization. These data[29] together with frequency sweep decoupling experiments were compatible

with the underlying structural features of 46 and 47.

Catalytic hydrogenation served to distinguish between these possibilities. When the isomerization product was reduced with 5% palladium on carbon in absolute ethanol, ethyl acetate, or tetrahydrofuran, two $C_{12}H_{20}$ compounds were produced in a constant ratio of 6.5:1. Because saturation of the double bonds in 47 can give rise only to a single hexahydro product, this triene can now be dismissed as the correct structure.

That 46 did indeed possess the indicated tricyclic skeleton was confirmed by the independent synthesis of its perhydro derivatives (50 and 51). One of the isomers had been previously described by Haworth and coworkers,[30] but unfortunately its infrared spectrum proved to be no longer available. However, catalytic hydrogenation of dienone 48[31] and subsequent Wolff-Kishner reduction of 49 furnished the same two hydrocarbons in a 1:1.3 ratio (Scheme V). The high resolution infrared and 100-MHz pmr spectra of the first components from the two reductions were superimposable. Elucidation of the relative stereochemistry of the isomeric pair was not attempted.
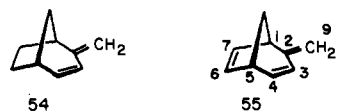
Scheme V
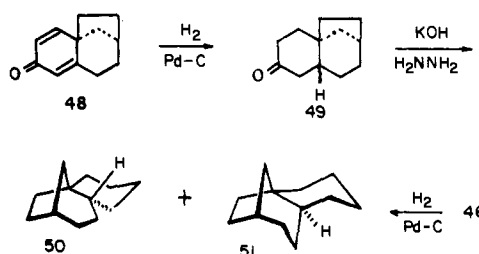
The analogous rearrangement of 11 led to the dideuterated counterpart of 46. The most revealing features of its 100-MHz pmr spectrum were the absence of two olefinic protons, one each from the δ 5.85–6.20 and 5.60–5.84 sets of 46, and simplification of the doubly allylic bridgehead hydrogen signal to a broadened triplet. Upon double irradiation of the C_8 methylene region (δ 1.8), the bridgehead proton absorption collapsed to a doublet ($J = 6$ Hz). The 4,6-d_2 and 3,7-d_2 isomers (cf. 46 for numbering) could thereby by excluded. Because the high field olefinic signal due to H_9 remains present, labeling at that site is also precluded. Were the deuterium atoms positioned at the 4,7 or 3,6 sites, then H_3 and H_7 should be displayed as unsplit or very weakly coupled peaks, but no simple pattern of this type is seen. To distinguish between the remaining two alternatives (52 and 53), information compiled from spin decoupling studies on 46 together with literature data for the parent bicyclo[3.2.1]octa-2,6-diene system[32] was submitted to LAOCOON III computer simulated analysis.[33] Although a close spectral match was achieved for 46 and 52, several minor differences in signal intensities discouraged us from concluding only on this basis that 52 was the actual isomerization product.

A definitive resolution of the question was achieved by cmr spectroscopy. Table I gives the carbon chemical shifts for 2-methylenebicyclo[3.2.1]oct-3-ene (54) and 2-methylenebicyclo[3.2.1]octa-3,6-diene (55),[34] the additional double bond in the latter causing C_2 and C_4 to appear at somewhat higher field. A similar phenomenon is observed in the bridged system 46, the alkyl chain further perturbing C_2 and C_9 in the expected manner.[35] In the deuterium-labeled product, significant loss of signal for the 136.1 and 133.3 ppm peaks is seen as a result of unbridled C–D coupling at C_6 and C_7. Structural assignment 52 is thereby confirmed.
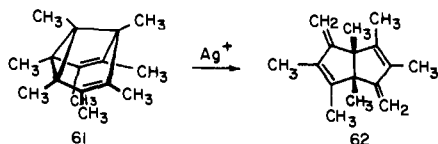

A grossly reasonable but untested mechanism for the rearrangement of 11 to 52 involves initial bonding of Ag^+ to a permanently olefinic carbon of the semibullvalene nucleus (Scheme VI). Either of the resulting homoallylic cations (56 or 58) can converge by minimum electron redistribution pathways to dicyclopropylcarbinyl species 57, the inherent stabilization in which is difficult to assess but may be sufficient to dismiss 56 and 58 as true intermediates. The hypothetical mechanism is completed by proton loss from 57 to give triene 59, protolytic cleavage of the C–Ag bond in which provides suitably labeled product and regenerates the catalytic agent.

Scheme VI

• denotes deuterium
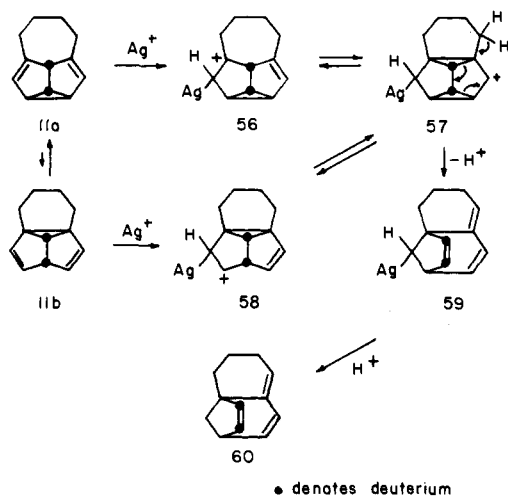
Prior to this work, Criegee and Askani obtained evidence that octamethylsemibullvalene (61) reacts with silver nitrate to produce tetraene 62.[2c] No explanation was advanced for this interesting transformation (note loss of two hydrogen atoms), but the seemingly divergent behavior of 61 relative to 5 did concern us for a time. Should the octamethyl derivative isomerize according to the mechanism considered above, the prevailing product should be tetraene 68 (Scheme VII). Yet it seemingly is not isolated. However, given the recent findings of Kusuya and Hart[36] who observed irreversible rearrangement of permethylated bicyclo[3.2.1]octadien-2-yl cation 63 to its bicyclo[3.3.0]octadien-2-yl counterpart 64 above −60° in FSO₃H/SO₂ClF,
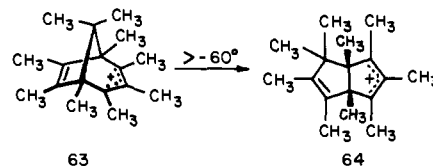
the possibility remains open that 68 does in fact intervene. In principle, rebonding of Ag^+ to 68 could generate the structurally related cation 69, operation of the same series of bond shifts in which would lead via 70 ultimately to 62. Substantiation of this suggestion must await the independent synthesis of 68.

Scheme VII
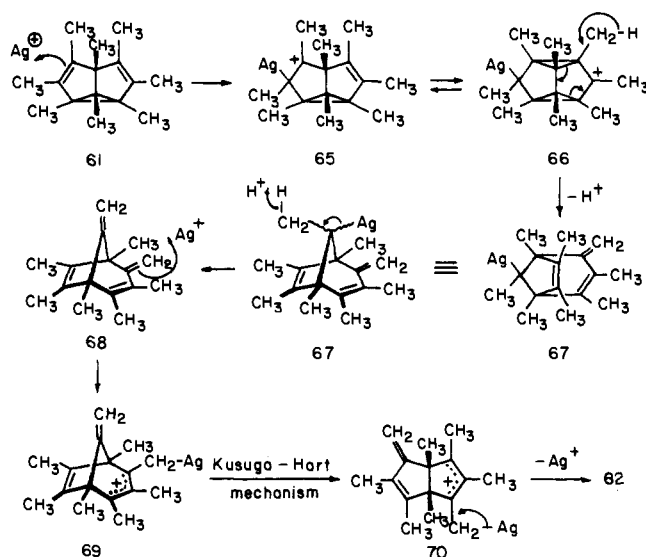
Conclusions

In summary, we conclude on the basis of the evidence herein presented that the semibullvalene nucleus possesses considerable latent reactivity. The inherent capacity for structural rearrangement is without doubt facilitated by alkyl substitution at suitable points in the molecular framework since in certain instances proton loss from these groups is evidenced. A number of important questions still remain to be answered about this system in general and about the influence of structural variation on photoexcited state reactivity in particular. Specifically, the question may now be posed concerning the possibility of a degenerate photoisomerization of semibullvalene itself. Is the C_8H_8 structure capable of di-π-methane conversion to barrelene which can then return to semibullvalene by the demonstrated mechanism to give positionally scrambled product? This extrapolation of our findings awaits suitable experimental test.

Experimental Section

Thermal Rearrangement of 5. A 90-mg (0.57 mmol) sample of 5[5c,10] was passed through a quartz chip-packed quartz tube heated at 500° by entrainment in a stream of dry nitrogen (1.0 mm). The residence time was 1–2 sec. The effluent material was collected at −78° in a small U tube. There was obtained 62 mg (69%) of 6

Table I. Cmr Chemical Shift Data

Compd	C_2	C_3, C_4	C_6, C_7	C_9	Tetrahedral carbons
54	153.0	127.2, 138.1		106.2	31.2, 34.0, 36.3, 37.6, 43.3
55	144.5	126.1, 130.7	134.4, 138.4	110.3	40.7, 44.9, 48.6
46	137.7	126.0,[a] 132.0	133.3, 136.1	125.4[a]	20.4, 26.1, 32.6, 41.4, 48.6, 50.4
52	137.7	126.0,[a] 132.0	b	125.4[a]	20.4, 26.1, 32.6, 41.2, 48.6, 50.4

[a] May be interchanged. [b] Signals greatly diminished and split due to C–D coupling.

which was purified further by preparative vpc at 80° (4 ft × 0.25 in. 5% SF-96 on Chromosorb G) and shown to exhibit spectra identical with those of an authentic sample.[10,11]

N-Phenyltriazolinedione Addition to 7. To a magnetically stirred solution of 3.16 g (19.7 mmol) of **7**[11] in 90 ml of acetone cooled to −78° was added dropwise an acetone solution of N-phenyltriazolinedione until a slight red color persisted. Work-up as described for the protio example[5c] afforded 4.92 g (74.3%) of **8**: δ_{TMS} (CDCl$_3$) 7.45 (m, 5, aromatic), 6.23 (t, J = 4 Hz, 2, olefinic), 4.63 (t, J = 4 Hz, 2, >CH–N<), and 1.4–2.1 (br m, 8, methylenes). The cyclobutene singlet at 5.95 was lacking.

Photocyclization of 8. A solution of 4.92 g (14.6 mmol) of **8** in 700 ml of acetone was irradiated through Vycor with a 200-W Hanovia lamp for 2.5 hr. The yield of **9** after chromatography on alumina was 4.82 g (98.0%): δ_{TMS} (CDCl$_3$) 7.50 (br m, 5, aromatic), 4.66 (t, J = 3.5 Hz, 2, >CH–N<), 3.58 (m, 2, methine), and 1.4–2.0 (m, 8, methylenes). The methine multiplet at δ 2.98 was not in evidence.

Ag$^+$-Catalyzed Rearrangement of 9. Reaction of 4.82 g (14.3 mmol) of **9** with silver nitrate in aqueous methanol as previously described[5c] afforded a quantitative yield of white crystalline **10**: δ_{TMS} (CDCl$_3$) 7.30–7.73 (br m, 5, aromatic), 4.88 (br t, J = 2.7 Hz, 2, >CH–N<), 1.67–2.30 (br m, 6, proximate methylenes and cyclopropyl), and 0.92–1.50 (br m, 4, remote methylenes).

2,8-Tetramethylenesemibullvalene-1,5-d$_2$ (11a ⇌ 11b). To a 100-ml three-necked flask were added 1.09 g (3.28 mmol) of **10**, 25 ml of isopropyl alcohol, and 2.11 g (33 mmol) of potassium hydroxide, and the mixture was blanketed with nitrogen. After being heated at reflux for 1 hr, the dark yellow solution was cooled to 0°, treated with 3 N hydrochloric acid until pH 2, and stirred for 5 min. The pH was then adjusted to 8 with 3 N ammonium hydroxide, and pentane (15 ml) together with methylene chloride (15 ml) was added. To this mixture was added 2.88 g (33 mmol) of activated manganese dioxide, stirring was maintained for 3 hr at 25°, and the insolubles were removed by filtration through Celite. The pale yellow filtrate was washed with water and brine, dried, and carefully distilled at atmospheric pressure to remove solvents. Preparative vpc isolation at 85° (3.5 ft × 0.25 in. 5% SF-96 on Chromosorb G) furnished 280 mg (53.4%) of **11**: δ_{TMS} (CDCl$_3$) 4.82 (br s, 2, olefinic), 2.64 (br s, 2, cyclopropyl), 2.11–2.51 (br m, 4, allyl), and 1.18–1.78 (br m, 4, remote methylenes).

Thermal Rearrangement of 11. A freshly purified 280-mg sample of **11** was pyrolyzed as above at 460° (1.5 mm). The collected liquid was subjected to preparative vpc at 95° [3.5 ft × 0.25 in. 5% PMPE (five-ring) on Chromosorb G] to separate unreacted **11** (81 mg) from **12** (51 mg, 26%).

TCNE Adduct of 12. The deuterium labeled cyclooctatetraene **12** (51 mg, 0.319 mmol) and tetracyanoethylene (407 mg, 3.19 mmol) dissolved in ethyl acetate (15 ml) were heated at reflux under nitrogen for 5 hr. The resulting light red solution was cooled, diluted with ether, washed with 10% sodium bisulfite solution, water, and brine, and dried. Solvent removal left a yellow solid which was chromatographed on Florisil (elution with methylene chloride) to give 40 mg (44%) of adduct **13** as a white solid: δ_{TMS} (acetone-d$_6$) 6.5 (br d, J = 8 Hz, 1, olefinic), 4.0 (dd, J = 4.5 and 2 Hz, 2, bridgehead), 3.3 (br m, 1, cyclobutenyl sp^3 center), 1.84 (br m, 4, allyl), and 1.6 (br m, 4, methylenes). See text for further discussion of pmr data.

Photoisomerization of 5. Into each of seven base-washed 20-ml Pyrex test tubes were placed 23.6 mg of freshly purified **5** and 15 ml of reagent grade acetone. After each tube had been deaerated with a slow stream of dry nitrogen for 20 min, it was capped with a serum stopper and placed in a Rayonet "merry-go-round" unit which was equipped with 3000-Å lamps. After the solutions had been irradiated for 2 hr, they were combined, diluted with pentane,

washed with water, 5% aqueous ammonium hydroxide, water, and brine, and dried. Careful removal of the major portion of the solvent by atmospheric distillation was followed by preparative vpc separation at 100° [the 5% PMPE (five-ring) column]. There were recovered 41.4 mg of unrearranged **5** and 7.7 mg (6.2%) of **24a** ⇌ **24b**: λ_{max} (isooctane) 235 sh nm (ε 3200); δ_{TMS} (CDCl$_3$) (35°) 5.4 (d, J = 6 Hz, 1, H$_8$), 5.14 (dd, J = 6 and 2 Hz, 1, H$_7$), 4.72 (br s, 1, H$_3$), 2.75 (d, J = 5 Hz, 2, H$_4$ and H$_6$), 2.55 (t, J ≈ 6 Hz, 1, H$_5$), 2.3 (m, 2, allyl), and 1.2–1.9 (m, 6, methylenes); calcd m/e 158.1095, found 158.1098.

Photoisomerization of 11. Into each of eight base-washed Pyrex test tubes were placed 25.2 mg of **11** and 10 ml of acetone. Irradiation as above for 2.5 hr and analogous work-up gave 12.6 mg (8.4%) of **26** and 55 mg of recovered starting material: δ_{TMS} (CDCl$_3$) 5.4 (m, 0.47), 5.14 (d, J = 5 Hz, 0.47), 4.72 (br s, 1), 2.75 (d, J = 5 Hz, 1.69), 2.55 (t, J ≈ 6 Hz, 0.83), 2.3 (m, 2), and 1.2–1.9 (m, 6).

Alumina-Promoted Rearrangement of 5. A 425-mg sample of **5** was slowly eluted (pentane) through a column of neutral activity I alumina (ca. 300 g), and the eluate was carefully concentrated at atmospheric pressure to leave 417 mg of a new hydrocarbon identified as **38**. An analytical sample was obtained by preparative vpc isolation at 80° (the 5% SF-96 column): δ_{TMS} (CDCl$_3$) 5.95 (s, 2, H$_3$ and H$_4$), 5.67 (m, 1, H$_7$), 5.15 (m, 1, H$_9$), 3.42–4.08 (m, 2, H$_1$ and H$_5$), and 1.0–2.9 (series of m, 8, allylic and methylenes); λ_{max} (isooctane) 236 (ε 14,000), 243 (14,000), and 262 sh nm (5600); calcd m/e 158.1095, found 158.1093.

Anal. Calcd for C$_{12}$H$_{14}$: C, 91.08; H, 8.92. Found: C, 91.13; H, 8.79.

Alumina-Promoted Rearrangement of 11. A partially polymerized sample of **11** (56 mg) was eluted through alumina (17 g) as before. Collection of monomeric rearranged product by preparative vpc methods furnished 10.8 mg of **41**: δ_{TMS} (CDCl$_3$) 5.95 (s, 2), 5.67 (t, J = 7 Hz, 1), 5.15 (m, 1), and 1.0–2.9 (series of m, 8).

Magnesium Bromide Promoted Rearrangement of 5. A solution of anhydrous magnesium bromide in ether was prepared by the addition of 1.80 g (9.6 mmol) of 1,2-dibromoethane in 25 ml of ether dropwise to 0.25 g (10 mg-atoms) of reagent grade magnesium turnings in 75 ml of ether at the reflux temperature. After being heated for 6 hr, the solution was filtered and stored at 0° under nitrogen.

To a magnetically stirred solution of 22 mg (0.14 mmol) of **5** in 10 ml of anhydrous ether was added 10 ml of the above solution. After 15 min, water and pentane were added, and the organic layer was separated, washed, and dried. Removal of the solvent in vacuo left **38** in quantitative yield. Identification was made by spectral comparisons.

Rhodium Dicarbonyl Chloride Dimer-Catalyzed Isomerization of 5. To a solution of 40 mg of **5** in 300 μl of deuteriochloroform contained in an nmr tube was added 6 mg of rhodium dicarbonyl chloride dimer. The mixture was placed in a constant-temperature bath maintained at 40° while protected from light, and the pmr spectrum was periodically recorded. After a total of 114 hr, no signals due to **5** remained; vpc isolation gave 5 mg of **38** as the only volatile product.

Catalytic Reduction of 38. A mixture of **38** (38 mg), 5% rhodium on carbon (38 mg), and anhydrous tetrahydrofuran (5 ml) was exposed to a hydrogen atmosphere at ambient pressure. After the initial hydrogen consumption had subsided, glacial acetic acid (5 ml) was introduced via syringe, and stirring was continued for 8 hr. The filtered solution was diluted with water, extracted with pentane, dried, and concentrated. Preparative vpc at 90° [the 5% PMPE (five-ring) column] afforded two components in a ratio of 1:49 (for the major product: calcd m/e 164.1565, found 164.1567). This material was identical with the major reduction product of

5.[5c]

Ag⁺-Catalyzed Isomerization of 5. To a magnetically stirred solution of 145 mg (0.917 mmol) of 5 in 6 ml of anhydrous benzene was added dropwise 10 ml of 0.2 N silver perchlorate-benzene solution. After 30 min in the absence of light and atmospheric moisture, the solution was washed with dilute ammonium hydroxide solution, water, and brine and dried. Careful solvent removal left a dark oil, preparative vpc of which at 80° (the 5% SF-96 column) afforded 65 mg (45%) of 46 as a colorless oil: λ_{max} (isooctane) 243 nm (ϵ 12,000): δ_{TMS} (CDCl₃) 5.88–6.25 (m, 2, H_4 and H_6), 5.6–5.8 (m, 2, H_3 and H_7), 5.44 (t, J = 3.2 Hz, 1, H_9), 2.73–3.05 (m, 1, H_5), 1.98–2.30 (m, 2, allyl), and 1.42–1.92 (m, 6, methylenes); calcd m/e 158.1095, found 158.1095.

Anal. Calcd for C₁₂H₁₄: C, 91.08; H, 8.92. Found: C, 90.87; H, 9.06.

Catalytic Hydrogenation of 46. A solution of 46 (51.1 mg) in absolute ethanol (7 ml) containing 153 mg of 5% palladium on carbon was hydrogenated at 1 atm for 1 hr. Vpc analysis revealed the formation of two products in a 6.5:1 ratio. The major component was isolated by preparative vpc (11.5 ft × 0.25 in. 8% Carbowax 20 M on Chromosorb G) and shown to be identical with the minor product from the Wolff-Kishner reduction of 49: calcd m/e 164.1565; found m/e 164.1567.

Reduction of 48. A solution containing 396 mg (2.3 mmol) of 48[31] in 20 ml of ethyl acetate was hydrogenated over 255 mg of 5% palladium on charcoal at 1 atm for 2 hr. Filtration and solvent removal left 354 mg (86.5%) of 49 as a colorless oil: ν_{max} (neat) 1725 cm⁻¹.

Anal. Calcd for C₁₂H₁₈O: C, 80.85; H, 10.18. Found: C, 81.22; H, 10.34.

Wolff-Kishner Reduction of 48. A 110-mg (0.621 mmol) sample of 48 was heated under nitrogen with 2.6 ml of triethylene glycol, 0.76 ml of hydrazine hydrate, and 102 mg of hydrazine dihydrochloride for 4 hr at 130°. Potassium hydroxide (340 mg) was added, and the temperature was slowly raised to 210° while the volatile materials were distilled through a 6-in. Vigreux column. After 3 hr at 200–210°, the reaction mixture was processed in accepted fashion and the residual oil was subjected to preparative vpc (the Carbowax 20 M column). Two components in the ratio 1:1.3 were isolated in quantities sufficient for high resolution infrared and 100-Hz pmr analysis: δ_{TMS} (CDCl₃) 2.1 (m, 1) and 0.8–2.0 (m, 19).

*Anal.* Calcd for C₁₂H₂₀ (two-component mixture): C, 87.73; H, 12.27. Found: C, 87.58; H, 12.27.

Ag⁺-Catalyzed Isomerization of 11. A 105-mg (0.651 mmol) sample of 11 was treated as above with 3.5 ml of 0.2 N silver perchlorate-benzene solution at ambient temperature for 1 hr. The analogous work-up gave 32 mg (30%) of 52: δ_{TMS} (CDCl₃) 6.0 (dd, J = 8 and 5 Hz, 1), 5.6 (d, J = 7.5 Hz, 1), 5.44 (t, J = 3.2 Hz, 1), 2.84 (t, J = 5 Hz, 1), 2.2 (br m, 2, allyl), and 1.4–2.0 (br m, 6. methylenes).

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(13) We acknowledge with appreciation the invaluable assistance of Professor R. J. Ouellette in the computer simulation work.
(14) This shift must occur on the periphery of 15 rather than in the internal part of the structure since migration in the latter sense gives i which cannot in turn provide 12.

i
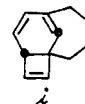
(15) More specifically, the need to postulate superimposed chemical shifts for H_5 and H_6 is incompatible with existing data on 1,3-dimethylsemibullvalene.[2m,9a] Also, as the temperature of the system is decreased, H_8 (assumedly at δ 5.6) is forced to become more olefinic in character (downfield shifting), while the C_5–H and C_6–H bonds must necessarily gain p character. This means that the concentration level of 23a must increase with a drop in temperature, a consequence of which is that H_2 (assumedly at δ 4.9) should shift to lower field to an extent approximating the displacement of the H_8 signal. It does not.
(16) A fourth possible isomer ii has been dismissed from the outset, because it incorporates a highly strained *trans*-cycloheptene moiety.

ii
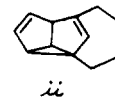
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Phenyl Nitrene. A Flash Photolytic Investigation of the Reaction with Secondary Amines[1a]

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Abstract: The flash photolysis of aryl azides in the presence of secondary amines, which serve as nucleophilic trapping agents, has been studied. As in steady illumination photolyses under similar conditions the major reaction products are 2-dialkylamino-3H-azepines. The kinetics of the reactions of dibutylamine (DBA) with the intermediate generated by photolysis of phenyl azide and its o-methyl, o-ethyl, and o-trifluoromethyl analogs have been measured. The rates are sensitive both to solvent and the aryl substituent and fall in the range 10^4–10^9 l. mol^{-1} sec^{-1}. The intermediate which reacts with DBA is not believed to be the nitrene but a species derived therefrom, most likely a strained closed-shell azirine. This intermediate does not absorb strongly above 300 nm and has a lifetime of ~5 msec in the unsubstituted system in the absence of an amine. Formation of the final 3H-azepine proceeds through the 1H tautomer and rates for uncatalyzed and dibutylammonium ion catalyzed tautomerism are reported for the unsubstituted o-methyl and o-trifluoromethyl compounds. Activation data are recorded for several of the reactions. An apparent negative E_a is observed for the reaction of the intermediate from phenyl nitrene and DBA.

Phenyl nitrene exhibits little of the reactivity commonly associated with nitrene or carbene intermediates. It gives neither efficient intermolecular insertion reactions with saturated hydrocarbons[2] nor addition to olefins or benzene.[3] Such processes do occur in intramolecular thermal reactions.[4] Two factors have been suggested to be responsible for the apparent lack of reactivity. The nitrene may be in equilibrium with a closed shell azirine B.[5] Loss of nitrene
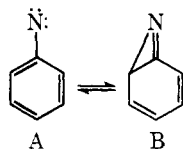

reactivity might also be the result of a large contribution to the structure by the dipolar resonance form A′ which would diminish the electron deficiency at nitrogen.[10] Support for
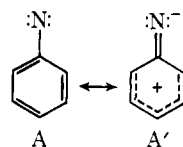
this proposal can be drawn from the tendency for nitrene reactivity to be accentuated in systems with electron attracting aryl substituents.[11] The two factors are not mutually exclusive.

Interest in phenyl nitrene is further enhanced by studies of gas phase pyrolyses which suggest rearrangements to azacycloheptatrienylidene (C) and pyridyl carbene (D).[12]
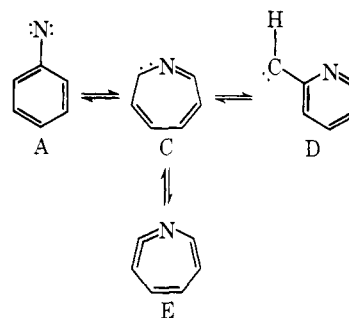
Related studies of structural isomerizations of aryl carbenes in the gas phase and in solution also suggest the possibility of a strained ketenimine structure.[13] Recent efforts aimed at using photolysis of azido groups to mark biological active sites[14] provided an additional impetus for developing a firm mechanistic understanding of aryl nitrene intermediates.

Previous studies of phenyl nitrene have been directed at the triplet species, and the esr[15] and ultraviolet spectrum[16] have been reported. As our work neared completion a study of phenyl nitrene by flash photolysis in the gas phase was reported.[17] The only process which was firmly identified was reaction of triplet nitrene with phenyl azide to give azobenzene. This reaction accounts for only a fraction of the phenyl azide, however, since the yield of azobenzene is only 6%. These studies provide little basis for understanding the solution chemistry of phenyl nitrene since the species primarily involved in solution reactions is the singlet.[18,19]

The present study concentrates on the photolysis of aryl azides in the presence of secondary amines using the techniques of flash photolysis and fast kinetic spectroscopy. The