THE THERMOCHEMICAL BEHAVIOR OF SEMIBULLVALENES. ANNELATION

EFFECTS ON THE COURSE OF REARRANGEMENT

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Owing to its unique geometrical features, semibullvalene ($\underline{1a}$) commands a central position

as the molecule most readily capable of undergoing Cope rearrangement ($\Delta F^{\ddagger}_{calcd}$ = 2.3-3.6

kcal/mole).[1] With the development of more accessible routes to semibullvalenes[2] has arisen

an intensification of interest in the chemical properties of this intriguing cis-divinyl-

cyclopropane system. As a continuation of our exploration of the $(CH)_8$ energy surface,[3] the

pyrolysis of semibullvalenes has been examined and we now report findings of both synthetic

and mechanistic significance.

Heating samples of $\underline{1a}$ (diluted with nitrogen) in a flow system for short contact times

(1-3 sec) at a temperature of 427° and 30 mm pressure led with good recovery to cyclooctate-

traene ($\underline{2a}$) as the only product. The 1,5-dimethylsemibullvalane molecule ($\underline{1b}$),[2f] in which

two carbon atoms of the $(CH)_8$ framework are now labeled by virtue of methyl substitution, was

$\underline{1a}$, R = H
$\underline{1b}$, R = CH_3

$\underline{2a}$, R = H
$\underline{2b}$, R = CH_3

$\underline{3}$
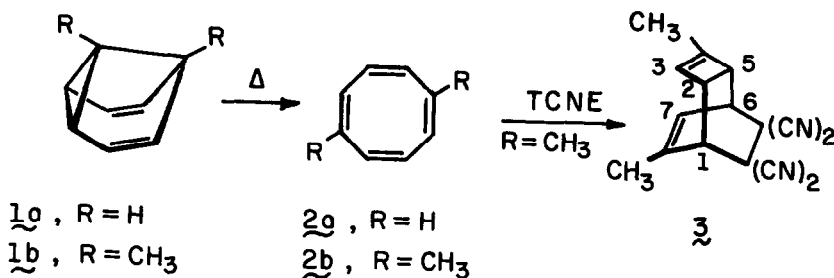
similarly pyrolyzed at 390°. In this instance, a lone yellow hydrocarbon[4] was obtained (71%

yield) whose nmr spectrum ($CDCl_3$) consisted of three absorptions: a pseudosinglet of area 4

at δ 5.68, a narrow multiplet (2H) at 5.52, and a six-proton singlet at 1.72. The ultra-

violet and infrared absorptions of this product, although compatible with a dimethylcyclo-

octatetraene structure, were not those of the 1,2- or 1,4- derivative.[3b] Treatment with

tetracyanoethylene in refluxing ethyl acetate gave, however, an adduct ($\underline{3}$, mp 179.5-180°),[4]

nmr analysis[5] of which requires the product to be that derived from (4 + 2) cycloaddition to

1,5-dimethylcyclooctatetraene (2b). When conducted on a preparative scale, the thermal re-
arrangement of 1b represents a convenient and attractive method for the synthesis of 2b. This
procedure should be generally applicable to other 1,5-disubstituted cyclooctatetraenes, thus
providing a direct route to such isomers which has not heretofore been available.

As to mechanistic detail, the conversion of 1 to 2 can be concisely represented in terms
of the often discussed[6] bicyclo[3.3.0]octadienediyl intermediate (4, Scheme I). At the
temperatures employed herein, these thermally activated diradicals acquire sufficient energy
to experience homolytic cleavage of the central bond with resultant 1,5 positioning of the R
groups in 2.[7]

Scheme I
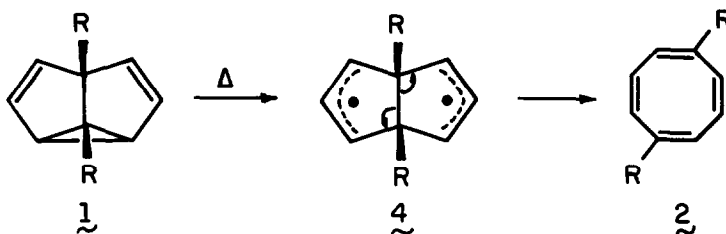
In an attempt to introduce mechanistic bias, the tetramethylene bridged semibullvalene
5a ⇌ 5'a, prepared by an adaptation of our earlier synthetic route,[2d,8] was subjected to
pyrolysis. Strict adherence by this hydrocarbon to rearrangement by Scheme I would lead to a
severely strained 1,3 annelated cyclooctatetraene. In gas-phase experiments conducted at
460-500° and 1.5 mm, 5 did afford a cyclooctatetraene product (69% yield). This material was
identified, however, as 6[3a,9] on the basis of its spectral characteristics and conversion to
the TCNE adduct. This transformation is of particular interest for it consists not only of
the predescribed ring opening, but also in the concurrent transposition of the 1,3 bridge
in 5a ⇌ 5'a to a 1,2 tetramethylene chain in 6.

Diels-Alder addition of N-phenyltriazolinedione to the known 11,12-dideuterio[4.4.2]-
propella-2,4,11-triene[3a] followed by acetone-sensitized photocyclization, silver(I) catalyzed
rearrangement, hydrolysis, and oxidation gave 5b ⇌ 5'b. The samples of 1,2-tetramethylene-
cyclooctatetraene-d_2 obtained from pyrolysis of this labelled semibullvalene were separated
from unrearranged 5b ⇌ 5'b by preparative vpc and converted directly to the TCNE adducts.
Their nmr spectra revealed the absence of an sp³-bound proton in the cyclobutene ring and a

$$5 \qquad\qquad 5' \qquad\qquad 6$$

a, R = H ; b, R = D
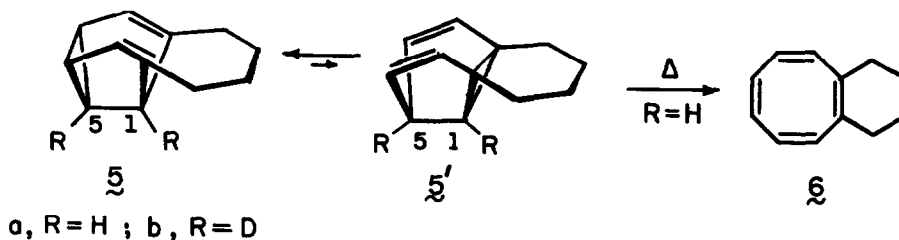
hydrogen from the pair H_7, H_8. The problem of distinguishing between 7 and 8 was resolved by making recourse to a LAOCOON III computer program to simulate the 100 MHz nmr spectra of 7 and 8.[10] By this technique, it was found that the combined absorption due to H_1 and H_8 differs markedly in the two isomers and that the spectra of the isolated labeled adduct conformed to the pattern uniquely compatible for 8. Consequently, the annelated cyclooctatetraene obtained from 5b ⇌ 5'b is isotopically substituted predominantly, and perhaps exclusively, as in 9.

$$7 \qquad\qquad 8 \qquad\qquad 9$$
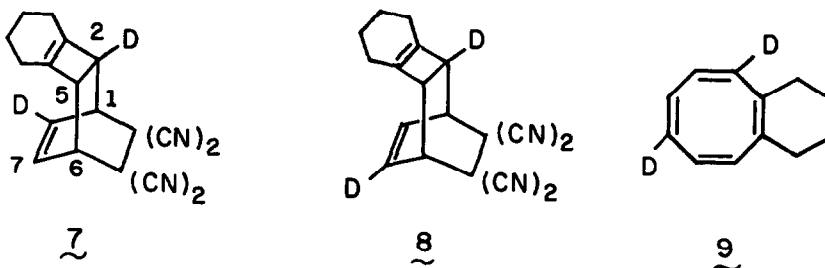
The 1,4-disposition of the deuterium atoms in 9 requires that C_1 in 5b ⇌ 5'b ultimately become transposed with one of the adjacent bridgehead carbon atoms. These findings are not incongruent with the initial formation of the 1,3-annelated cyclooctatetraene 10 and in fact are fully consistent with expectations based upon its excessive ground state strain which would provide the driving force for conversion via 10 and 11 to the observed polyolefin (Scheme II). The involvement of bishomobenzene 11 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[3a] and in the thermal rearrangement reactions of cyclooctatetraenes.[3b]

Scheme II

● denotes deuterium
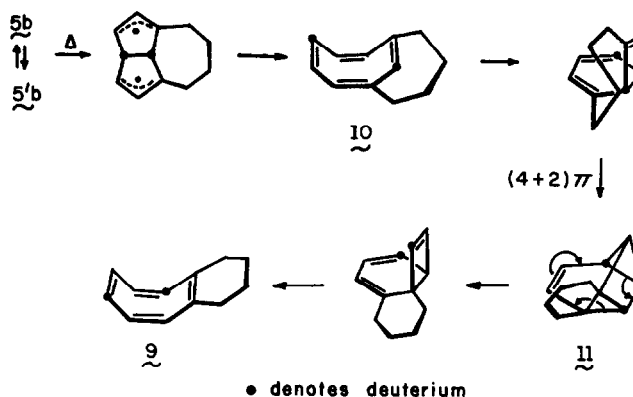
FOOTNOTES AND REFERENCES

1. (a) H.E. Zimmerman and G.L. Grunewald, J. Amer. Chem. Soc., 88, 183 (1966); H.E. Zimmer-
    man, R.W. Binkley, R.S. Givens, G.L. Grunewald, and M.A. Sherwin, ibid., 91, 3316
    (1969); (b) M.J.S. Dewar and W.W. Schoeller, ibid., 93, 1481 (1971); (c) M.J.S. Dewar
    and D.H. Lo, ibid., 93, 7201 (1971); (d) R. Hoffmann and W.-D. Stohrer, ibid., 93, 6941
    (1971); (e) The activation barrier to rearrangement in octamethylsemibullvalene is 6.4
    kcal/mol: F.A.L. Anet and G.E. Schenk, Tetrahedron Lett., 4237 (1970).
2. (a) H.E. Zimmerman and H. Iwamura, J. Amer. Chem. Soc., 90, 4763 (1968); (b) J. Meinwald
    and D. Schmidt, ibid., 91, 5877 (1969); (c) H.E. Zimmerman, J.D. Robbins, and J. Schantl
    ibid., 91, 5878 (1969); (d) L.A. Paquette, ibid., 92, 5766 (1970); (e) R. Askani,
    Tetrahedron Lett., 3349 (1970); (f) R. Askani, ibid., 447 (1971); (g) R.M. Moriarty,
    C.-L. Yeh, and N. Ishibe, J. Amer. Chem. Soc., 93, 3085 (1971).
3. (a) L.A. Paquette and R.E. Wingard, Jr., ibid., 94, 4398 (1972); (b) L.A. Paquette,
    R.H. Meisinger, and R.E. Wingard, Jr., ibid., 94, 9224 (1972).
4. Satisfactory combustion data have been obtained for all new compounds described herein.
5. Derived from spin decoupling studies at 100 MHz: H_1 (δ 3.60, m); H_2 (3.13, br m); H_3
    (5.61, m); H_5 (3.13, br m); H_6 (3.80, dd, J=7.0 and 3.0 Hz); H_7 (6.00, d with fine
    splitting, J=7.0 Hz).
6. For a summary of the reactions in which this radical is a probable intermediate, see
    J. Meinwald, D. Schmidt, and H. Tsuruta, J. Amer. Chem. Soc., 91, 5877 (1969). For more
    recent discussion, consult W.T. Borden and A. Gold, ibid., 93, 3830 (1971); M.J. Gold-
    stein and R. Hoffmann, ibid., 93, 6193 (1971).
7. As with other disubstituted cyclooctatetraenes,[3b] 2b undergoes thermally induced bond
    relocation in its own right. However, somewhat more elevated temperatures are required
    to achieve this end result.
8. L.A. Paquette, R.E. Wingard, Jr., and R.K. Russell, J. Amer. Chem. Soc., 94, 4739 (1972).
9. L.A. Paquette, R.E. Wingard, Jr., and R.H. Meisinger, ibid., 93, 1047 (1972).
10. The parameters employed in the computer simulation were derived from the unlabeled
    adduct and are as follows: $H_{2,5}$ = δ 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; and all other coupling constants equal zero. The invaluable assistance of Professor
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