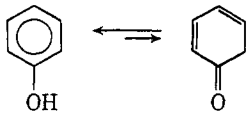
Table I. Observed and Calculated (INDO) Isotropic Hyperfine Coupling Constants of the Phenol Anion Radicals (in gauss)

	Proton				
	H(2)	H(3)	H(4)	H(5)	H(6)
Obsd	(+)43.8	(−)12.5		(−)12.5	
Calcd	+46.9	−8.7	+3.0	−4.9	−0.5

It is well known that the enol–keto tautomerism of phenol is almost entirely on the enol side, and phenol as such is considered a good electron donor (*e.g.*, its



ionization potential = 8.5 eV). On the other hand, a carbonyl group linked to a conjugated system is known to behave as a good electron acceptor.[7] Thus, the somewhat unexpected structure of the phenol anion can be understood as a manifestation of the effect of an extra electron upon the enol–keto tautomerism of the phenol molecules.

---

(7) See, for example, A. Szent-Gyorgyi, "Bioelectronics," Academic Press, New York, N. Y., 1968.

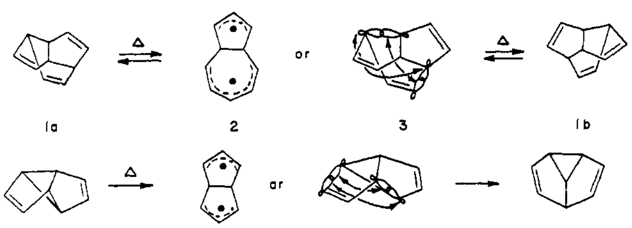
Paul H. Kasai,* D. McLeod, Jr.
Union Carbide Corporation, Tarrytown Technical Center
Tarrytown, New York 10591

Received May 1, 1972

Degenerate Thermal Rearrangement of Bicyclo[5.3.0^{4,8}]deca-2,5,9-triene (Lumibullvalene[1])

Sir:

Not infrequently, degenerate rearrangements remain undetected for substantial periods of time since, in the absence of suitable labeling, the individual compounds in question appear chemically unchanged. The title hydrocarbon **1** is a case in point. This $(CH)_{10}$ isomer was first isolated by Jones,[2] who described its clean transformation to *cis*-9,10-dihydronaphthalene at temperatures above 280°. It was not until two benzo analogs of **1** were shown to be in thermal equilibrium[3] that the propensity of **1** for degenerate rearrangement could be foretold.

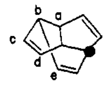


1a 2 3 1b

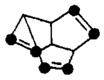
4 5 6 7

Goldstein and Hoffmann[4] have recently predicted that should this degenerate transformation be observed, it would be significantly slower than the already discovered[5] irreversible conversion of **4** to semibullvalene (**7**). The basis for their contention lies in the fact that irrespective of whether these interconversions proceed by concerted $[_\sigma 2_s + {}_\sigma 2_a]$ (*cf.* **3** and **6**) or stepwise diradical (*cf.* **2** and **5**) pathways, **1** must pass through a destabilized 3^+5^- pericyclic transition state, while that for **4** is 3^+3^- and stabilized. Presently, we provide convincing confirmation of this relative rate difference and demonstrate further that the concerted process[4] is nonoperative in the case of **1**.

The mono- (**8**) and hexadeuterated (**9**) samples of



8

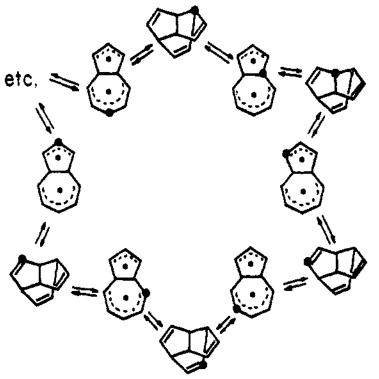


9

lumibullvalene (a solid circle represents the site of deuterium substitution) were prepared by the method of Katz[6] and by exchange of unlabeled **1** with lithium cyclohexylamide-d_1 in cyclohexylamine-d_2,[7] respectively.

Interestingly, degenerate thermal rearrangement of **8** under the control of orbital symmetry does not allow for *complete* carbon degeneracy. Although the sp^3-hybridized atoms would be subject to positional alternation, this fluctuation would be restricted to the aliphatic positions and would not result in "leakage" of the label to the olefinic sites. Such restrictions do not apply to the diradical process. Due to its C_2 symmetry axis, lumibullvalene possesses, *inter alia*, two identical a–b bonds. Homolytic cleavage of either leads to **2** which is endowed with a mirror plane of symmetry. As a result, π radical recombination by two equivalent modes may operate; a–b bonding returns unchanged starting material, whereas bond formation of type b–c provides the enantiomeric (and, in the case of **8** and **9**, deuterium scrambled) structure.[8] The possible nonconcerted degenerate cleavage and recombination pathways for **8** are summarized in Scheme I.

Scheme I



---

(1) Nomenclature introduced by L. T. Scott and M. Jones Jr., *Chem. Rev.*, **72**, 181 (1972).

(2) M. Jones, Jr., *J. Amer. Chem. Soc.*, **89**, 4236 (1967).

(3) L. A. Paquette, M. J. Kukla, and J. C. Stowell, *ibid.*, **94**, 4920 (1972).

(4) M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971).

(5) (a) J. Meinwald and D. Schmidt, *ibid.*, **91**, 5877 (1969); (b) J. Meinwald and H. Tsuruta, *ibid.*, **91**, 5878 (1969); (c) H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969).

(6) T. J. Katz and J. J. Cheung, *ibid.*, **91**, 7772 (1969).

(7) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969); H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 6096 (1968).

(8) The possibility exists that the diradical intermediate could recombine either a to d or c to e with formation of isobullvalene. However, the latter hydrocarbon is known[9] to isomerize rapidly *via* a Cope rearrangement to the molecules obtained by joining a to b or b to c.

(9) (a) K. Hojo, R. T. Seidner, and S. Masamune, *J. Amer. Chem. Soc.*, **92**, 6641 (1970); (b) T. J. Katz, J. J. Cheung, and N. Acton, *ibid.*, **92**, 6643 (1970).

It is to be noted that complete degeneracy arises after a minimum of four cleavages and recombinations of doubly allylic C–C bonds in one given direction. Because the indicated deuterium scrambling necessarily takes place in stepwise fashion (Scheme I), isotopic transposition to the remaining four pairs of carbon atoms in **8** is predicted to occur in the sequence b → a → c → e → d. The experimental findings (Table I) indicate that at least a prominent component, and possibly all, of the degenerate lumibullvalene rearrangement proceeds in the free-radical mode. Thus, positions a acquire deuterium label relatively rapidly as expected from the fact that carbons a and b become equivalent (excluding isotopic influences) after the first cleavage–recombination sequence. Difficulty was realized in achieving structural automerization which would position deuterium at carbons d because of the marked proclivity of the lumibullvalene molecule for conversion to *cis*-9,10-dihydronaphthalene under conditions which are relatively mild for such interconversions.[10] It is to be recalled that the d positions are not expected to acquire isotopic label until a minimum of four steps has been traversed (Scheme I).

Table I. Deuterium Atom Distribution in Pyrolyzed Samples of Monodeuteriolumibullvalene (**8**) (60 MHz, $CDCl_3$ Solutions)

Temp, °C	Pressure, mm	**8**:*cis*-9,10-dihydronaphthalene in pyrolysate, %	Rel deuterium atom distribution, %[a] a	b	c	d	e
240	12	100:0	7	93	1	0	0
290	30	45:55	30	48	11	0	11
310	30	60:40	28	47	9	5	9
280 (2×)[b]	25	60:40	32	28	28	0	12

[a] The percentage composition values were derived by careful integration of the various pmr absorptions (total area = 9 H), computation of the hydrogen count at each site, subtraction of these values from the maximum possible values (2 H), and multiplication of the numbers so obtained by 100. The chemical shifts of the various multiplets and their assignments are: c, δ 6.57; e, 5.81; d, 5.51; a, 3.10; b, 2.38. [b] Experiment conducted by preparative vpc separation of lumibullvalene from *cis*-9,10-dihydronaphthalene and repeat treatment under identical conditions.

Further experimentation[11] with **9** likewise attested to the capability of this $(CH)_{10}$ isomer to exchange its constituent sp^2- and sp^3-hybridized carbon atoms faster than irreversible conversion to *cis*-9,10-dihydronaphthalene (Table II). Should the conversion of **4** to semibullvalene (**7**) which proceeds with great facility at 25° [5] likewise occur by initial homolytic cleavage to give **5**,[12] the differing pericyclic constructs of **2** and **5** as defined by Goldstein and Hoffmann[4] could be the source of the significant energetic differences in the rate-determining steps of these closely related reactions.

Table II. Deuterium Atom Distribution in Pyrolyzed Samples of Hexadeuteriolumibullvalene (**9**) (60 MHz, $CDCl_3$ Solutions)

Temp, °C	Pressure, mm	**9**:*cis*-9,10-dihydronaphthalene in pyrolysate, %	Rel deuterium atom distribution, %[a] a	b	c	d	e
(Before pyrolysis)			0	0	38	36	27
285	18	79:21	8	3	33	31	25
300	20	58:42	9	7	29	30	25
300	20	58:42	11	7	28	29	24
312	18	37:63	16	13	24	25	21
320	18	30:70	18	13	24	24	21

[a] Calculations performed as before, assuming 5.98 protons per molecule (nmr and mass spectral data for **9**).

Acknowledgment. Partial support of this research by the National Science Foundation is acknowledged with appreciation.

---

(10) At the experimental level, only a very small temperature region (280–320°) was available which would allow return of sufficient lumibullvalene for characterization.

(11) All pyrolyses were conducted in the gas phase under a nitrogen atmosphere in a quartz tube packed with quartz chips as previously described: L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **93**, 2459 (1971).

(12) In this instance, the possible alternative operation of the concerted pathway remains to be established. See, however, H. M. Frey and R. G. Hopkins, *J. Chem. Soc. B*, 1410 (1970). Meinwald and Zimmerman[5] have proposed the diradical pathway in their original reports of this reaction (**4** → **7**).

Leo A. Paquette,* Michael J. Kukla
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received May 18, 1972

Book Reviews

Mass Spectrometry: Techniques and Applications. Edited by G. A. W. MILNE (National Heart and Lung Institute, National Institute of Health). Wiley-Interscience, New York, N. Y. 1971. x + 521 pp. $24.95.

This compendium consists of twelve chapters strongly oriented toward organic and biochemical mass spectrometry. The first 216 pages (seven chapters) are devoted to techniques: two on photographic and electric recording by Desiderio and by McMurray, one on GC–MS by Ryhage and Wikstrom, three on automated data acquisition and computer applications by Venkataraghavan, by Fennessey, and by Buchanan, Duffield, and Robertson; newer ionization techniques are discussed by Fales, with emphasis on chemical ionization. Applications chapters deal with peptides (Shemyakin, Yu A. Ovchinnikov, and A. A. Kiryushkin), stable isotopes in biochemistry (Grostic and Rinehart), problems in medicine and biochemistry (Milne), and fragmentation mechanisms (Bursey and Hoffman). The last chapter by Jennings is on metastable transitions and covers techniques and principles more so than uses. The overall caliber of the book is consistently high; only one chapter seems weak and there are several which could be termed outstanding in clarity, completeness, and levels of insight and expertise displayed.

There is little duplication in the chapters dealing with similar topics, and the editor has obviously done a very careful job in coordinating the book. Topical coverage is fairly complete within the restrictions of the intent of the book, which is very much defined by the preface which begins with "The affair between organic chemistry and mass spectrometry . . . ." About the only sub-