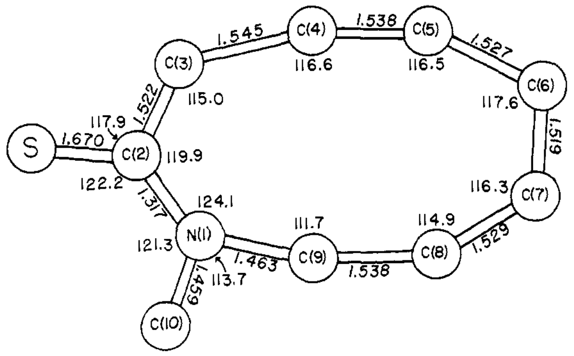

Figure 1. Bond lengths and bond angles for *N*-methylthiocapryllactam. Not intended to show actual molecular shape.

Table III. Torsional Angles for *N*-Methylcaprylthiolactam and *N*-Methyllaurylthiolactam

N-Methyllaurylthiolactam Angle	Deg	*N*-Methylcaprylthiolactam Angle	Deg
C(13)-N(1)-C(2)-C(3)	12.8	C(9)-N(1)-C(2)-C(3)	12.8
N(1)-C(2)-C(3)-C(4)	−95.7	N(1)-C(2)-C(3)-C(4)	−93.8
C(2)-C(3)-C(4)-C(5)	−173.5	C(2)-C(3)-C(4)-C(5)	90.4
C(3)-C(4)-C(5)-C(6)	−57.8	C(3)-C(4)-C(5)-C(6)	−100.5
C(4)-C(5)-C(6)-C(7)	−67.0	C(4)-C(5)-C(6)-C(7)	57.2
C(5)-C(6)-C(7)-C(8)	159.5	C(5)-C(6)-C(7)-C(8)	62.6
C(6)-C(7)-C(8)-C(9)	−74.7	C(6)-C(7)-C(8)-C(9)	−82.2
C(7)-C(8)-C(9)-C(10)	−78.2	C(7)-C(8)-C(9)-N(1)	−48.2
C(8)-C(9)-C(10)-C(11)	169.3	C(8)-C(9)-N(1)-C(2)	99.1
C(9)-C(10)-C(11)-C(12)	−62.7		
C(10)-C(11)-C(12)-C(13)	−55.5		
C(11)-C(12)-C(13)-N(1)	−178.5		
C(12)-C(13)-N(1)-C(2)	−102.4		

found in azacyclododecane hydrochloride (12-membered ring),[9] and six were found in 1,8-diazacyclotetradecane dihydrobromide (14-membered ring).[10]

There is an approximate dyad axis (with respect to torsion angles) in the ring skeleton of the lauryllactam passing through the center of the N(1)-C(2) bond and through C(8). There are no antiperiplanar partial conformations in the nine-membered ring. The torsion angles group around the synclinal conformation ($\omega \sim \pm 60°$) and ±100°, which is near the unfavorable anticlinal conformation ($\omega \sim \pm 120°$). The conformation of *syn*-*N*-methylthiocapryllactam is similar to that of one of the two independent molecules of cyclononylamine[11] which has one synperiplanar torsion angle of 26°.

The observed conformation of *N*-methylthiolauryllactam is very similar to the structure of one of the forms of dimethyl-1-hydroxycyclotridecyl phosphonate.[12] Both molecules have a string of nine successive torsional angles in common. Only the two atoms of the amido group occupy different relative positions.

Finally the conformation observed for *N*-methylthiocapryllactam is quite different from that observed for capryllactam itself (anti in crystal), but it is virtually identical with that of the protonated capryllactam (syn in crystal).[13,14]

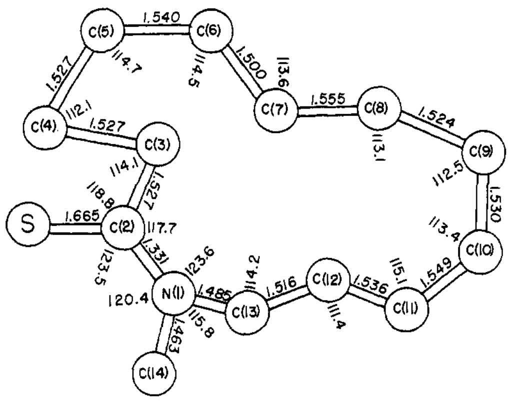

Figure 2. Bond lengths and bond angles for *N*-methylthiolauryllactam. Not intended to show actual molecular shape.

Large-membered *N*-methylthiolactams selectively crystallize into the enthalpically favored syn diastereomeric form, but undergo facile equilibration in solution at room temperature. This contrasts with the behavior of the analogous *N*-methyllactams in which the anti form predominates at equilibrium.[2] We explain this reversal on the basis of the greater steric size of sulfur relative to oxygen.[15]

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[9] J. D. Dunitz and H. P. Weber, *Helv. Chim. Acta*, **47**, 1138 (1964).

[10] J. D. Dunitz and E. F. Meyer, Jr., *ibid.*, **48**, 1441 (1965).

[11] R. F. Bryan and J. D. Dunitz, *ibid.*, **43**, 3 (1960).

[12] G. Samuel and R. Weiss, *Tetrahedron Lett.*, **33**, 2803 (1969).

[13] F. K. Winkler and J. D. Dunitz, *J. Mol. Biol.*, **59**, 169 (1971).

[14] We thank the referee for calling our attention to these two papers.

[15] For a discussion of the role of the steric effect of oxygen *vs.* sulfur in influencing the barrier heights to rotation in amides relative to thioamides see: W. Walter, E. Schaumann, and J. Voss, *Org. Magn. Resonance*, **3**, 733 (1971).

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Received May 10, 1972

Electron Spin Resonance Spectra of Phenol Anion Radicals Generated in Argon Matrices. Establishment of Their Ketonic Structure

Sir:

The possibility of generating and investigating the esr spectra of charged species within an argon matrix by means of the photoelectron transfer technique has been well established.[1] We report in this communication the esr spectra and their analyses of the phenol anion radicals generated by this technique.

Shown in Figure 1 is the esr spectrum obtained from an argon matrix containing Na atoms (0.1 atom %) and phenol (1 atom %) after it had been irradiated with yellow light ($\lambda > 5500$ Å) for 5 min. Prior to the photoirradiation, the matrix exhibited only the esr spectrum of the Na atoms.[2] The photoinduced signal in Figure

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[1] P. H. Kasai, *Accounts Chem. Res.*, **4**, 329 (1971). The details of the experimental procedures are described in this account also.

[2] C. K. Jen, V. A. Bowers, E. L. Cochran, and S. N. Foner, *Phys. Rev.*, **126**, 1749 (1962).

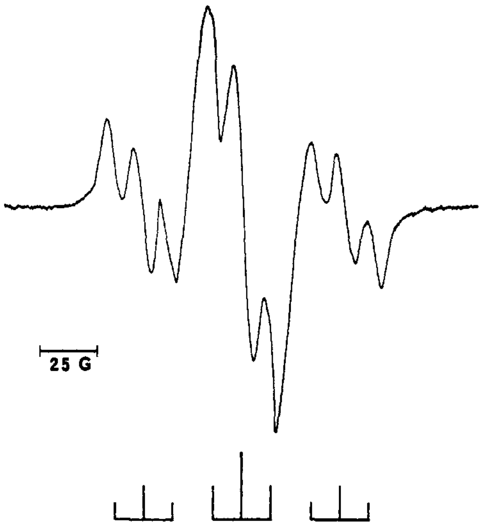
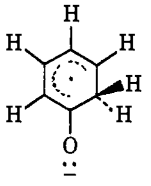


Figure 1. Esr spectrum of the phenol anion radicals generated in an argon matrix at ~4°K. The spectrometer frequency was 9.43 GHz.

1 is assigned to the phenol anion radicals produced by the electron-transfer process

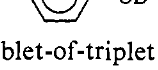
$$\mathrm{Na} + \mathrm{PhOH} \xrightarrow{h\nu} \mathrm{Na}^+ + [\mathrm{PhOH}]^-$$

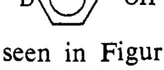
The triplet-of-triplet pattern indicated in the figure, however, signifies hyperfine structures which are clearly too large to be attributed to a π-anion radical retaining the planar structure of the neutral molecule. We propose that the observed spectrum be assigned to the anion of phenol in its ketonic form, I. Thus, the large



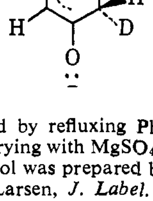
I

triplet with the spacing of 44 G is attributed to the protons at the carbon 2, projected respectively above and below the skeletal plane, and the small triplet with the spacing of 13 G to the protons 3 and 5 situated within the plane. Figures 2 and 3 are the spectra obtained when the experiment was repeated using the following monodeuterated species, respectively.[3,4]





The doublet-of-triplet pattern seen in Figure 2 is exactly that expected from the assignment proposed above and the structure



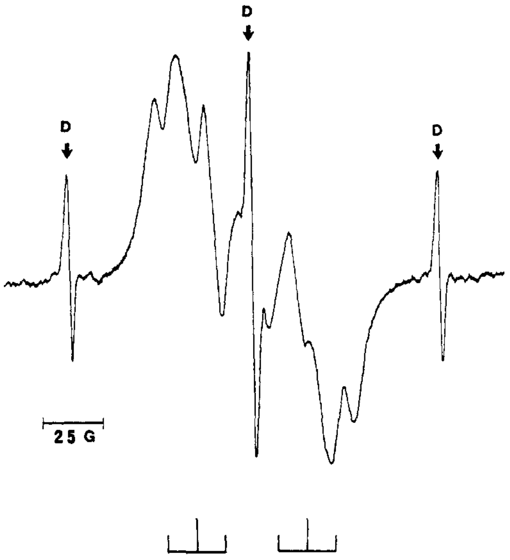


Figure 2. Esr spectrum of the monodeuteriophenol (Ph–OD) anion radicals generated in an argon matrix at ~4°K. The sharp triplet indicated by the arrows is due to D atoms.

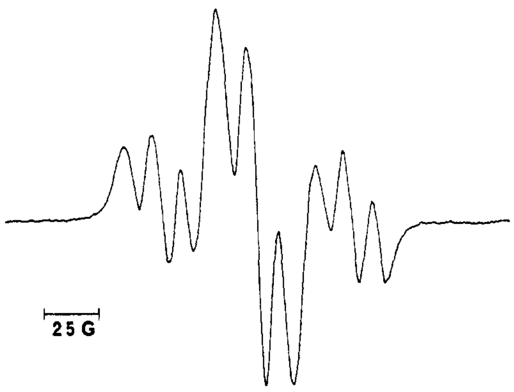


Figure 3. Esr spectrum of the *p*-deuteriophenol anion radicals generated in an argon matrix at ~4°K.

The hyperfine structures seen in Figures 1 and 2 could also result if the proton addition occurs at the para position. The triplet-of-triplet pattern in Figure 3 appears sharper but otherwise identical with that obtained with the nondeuterated species, indicating that the proton transfer occurs exclusively to the ortho position.

We believe that the proposed structure I results entirely from the intramolecular 1–3 transfer of the hydroxy proton for the following reasons: (1) only a mild radiation ($\lambda > 5500$ Å) is used for the generation of the anions; (2) only a trace amount of atomic hydrogen was detected in the matrix; and (3) no addition or transfer to the para position occurs.

Table I compares the observed hyperfine spacings with the isotropic hyperfine coupling constants calculated for the structure I by INDO molecular orbital calculation.[5] The agreement is reasonable.[6]

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(3) Ph–OD was prepared by refluxing PhOH in D_2O, followed by extraction with ether, and drying with $MgSO_4$.

(4) Para-deuterated phenol was prepared by the method described by T. Pedersen and N. W. Larsen, *J. Label. Compounds*, **5**, 195 (1969). The deuteration was confirmed to be >90% by its nmr spectrum and also by the esr spectrum of the phenoxide radicals generated in an argon matrix *via* ionization (P. H. Kasai and D. McLeod, Jr., unpublished results).

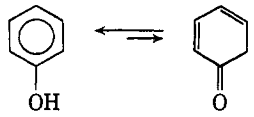
(5) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967); *J. Amer. Chem. Soc.*, **90**, 4201 (1968). The following structural parameters were used for the calculation: r_{C-C} = 1.4 Å, $r_{C-O} \approx$ 1.4 Å, r_{C-H} = 1.09 Å, ∠CCC = 120°, and ∠HCH = 109°.

(6) The coupling constants observed for a similar radical, cyclohexadienyl, are 47.5 G for the methylene protons and 10.4 G for both the ortho and para protons (H. Fischer, *Kolloid-Z.*, **180**, 64 (1962); S. Ohnishi, T. Tanei, and I. Nitta, *J. Chem. Phys.*, **37**, 2402 (1962)).

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.

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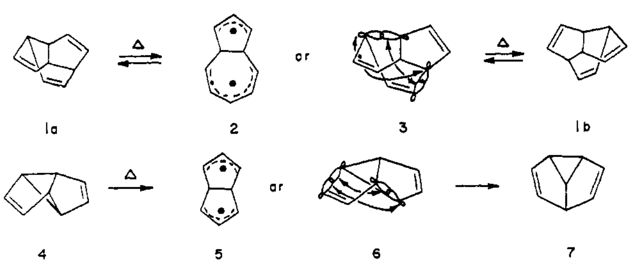
Degenerate Thermal Rearrangement of Bicyclo[5.3.0^{4,8}]deca-2,5,9-triene (Lumibullvalene[1])

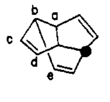
Sir:

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.



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



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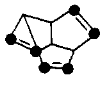

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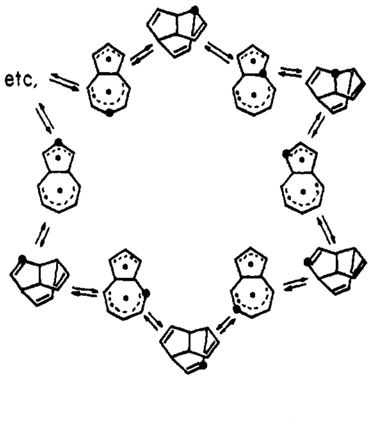
lumibullvalene (a solid circle represents the site of deuterium substitution) were prepared by the method of Katz[6] and by exchange of unlabeled **1** with lithium cyclohexylamide-d_1 in cyclohexylamine-d_2,[7] respectively.

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



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[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).