12   13
[4 + 1]   [4 + 2]⁺·

double bond (13). The complete proposed mechanism follows:

$$DP + Ar_3N^{+\cdot} \rightleftharpoons Ar_3N: + DP^+$$

$$DP^{+\cdot} + D \rightarrow A^{+\cdot}$$
$$A^{+\cdot} + DP \rightarrow A + DP^{+\cdot}$$ } propagation
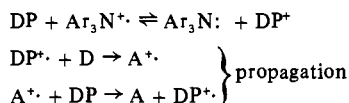
D = diene, DP = dienophile, A = adduct

The cation-radical Diels–Alder reaction appears to be of substantial synthetic, mechanistic, and theoretical interest. All of these aspects are currently being pursued. Potential applications to natural products synthesis seem especially promising.

Electronic Spin of the Ground State of m-Naphthoquinomethane, a Non-Kekulé Molecule with Nondegenerate Hückel Nonbonding Molecular Orbitals (NBMOs)

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A challenging experimental and theoretical problem in the study of biradicals[1] (or, more generally, of multiradicals) is the identification of the total electronic spin of the ground state. For those conjugated π systems in which a degeneracy or near degeneracy of singly occupied orbitals occurs,[2] qualitative theory customarily has invoked Hund's first rule,[3] which predicts the lowest energy state of a given electronic configuration to be the one of highest multiplicity. More recent theoretical approaches[4-6] suggest that violations of the rule may be expected in some cases.

Beyond that, no guidelines are available for systems in which approximate MO calculations do not show the required degeneracy. An important group of such molecules may be constructed hypothetically by heteroatom-for-carbon substitution in a non-Kekulé alternant hydrocarbon.[7] Two such examples have been realized experimentally. Platz and Burns[8] prepared 1-methylene-8-naphthiminyl (1) and concluded that it has a triplet ground state on the basis of a linear Curie plot of the intensity of the electron paramagnetic resonance (EPR) absorption over the temperature range 17–83.5 K. Our group,[9] by irradiation

1   2   3
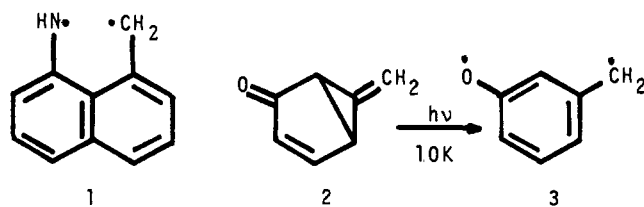
of 6-methylenebicyclo[3.1.0]hex-3-en-2-one (2) at 10 K, generated the EPR signal of a triplet and assigned to the carrier species the structure 3-methylenephenoxyl (m-quinomethane, 3) on the basis of its mode of synthesis and its zero-field splitting parameter, $|D|/hc = 0.0266$ cm⁻¹, a value which was in agreement with that calculated by a semiempirical method. However, the temperature range between the onset of serious saturation of the transitions (~15 K) and the irreversible disappearance of the signal (>40 K) was too narrow to permit an accurate determination of adherence to the Curie law. This prevented the assignment of the ground spin state.

We now report the synthesis and more complete characterization of the analogue 3-methylene-1-naphthoxyl (m-naphthoquinomethane, 4). This work substantiates the previously reported[9] structural assignment to 3 and provides information on the relative energies of the triplet and lowest singlet states of 4.

The synthesis of 4 is inherently simpler than that of 3, because the benzannelated ketal starting material 5[11] already is at the correct oxidation state to produce the precursor enone 6[10] (Scheme I).

Brief irradiation of a glassy (2-methyltetrahydrofuran) or polycrystalline (benzene) matrix of the enone 6 with a mercury arc at low temperature produces a bright orange color (compare the yellow color observed upon irradiation of 2). When the reaction is carried out in the cavity of a Varian E-9 EPR spectrometer (microwave frequency = 9.118 GHz), a signal characteristic[12] of a randomly oriented triplet species rapidly appears (Figure 1). In addition to the diagnostic weak $\Delta m_s = \pm 2$ transition near 1621 G, the spectrum shows a six-line $\Delta m_s = \pm 1$ pattern centered around 3250 G, which can be fitted to a spin Hamiltonian[13] with the zero-field splitting parameters (in cm⁻¹) $|D|/hc = 0.0204 \pm 0.0002$ and $|E|/hc = 0.0052 \pm 0.0004$.

The $|D|/hc$ value is significantly smaller than that observed[9] for the monocyclic diyl 3, as would be expected. Diyl 4 has a larger conjugated π system, which would favor a larger average separation of the unpaired electrons and hence a smaller spin–dipolar coupling. This comparison can be put on a quantitative basis by a calculation of the $|D|/hc$ value of 4 as 0.022 cm⁻¹, by using the same semiempirical approach we applied[9] to 3 (CNDO wave functions, neglect of a spin–orbit contribution to $|D|$, point-charge approximation, and scaling factor of 0.5). The agreement between the observed and calculated $|D|/hc$ values lends credence to the structural assignments to 3 and 4.[14]

Further support is provided by evidence that the carrier of the EPR signal has substantial spin density on oxygen. The spectrum of 4, like that of 3,[9] can be fitted only by the use of an anisotropic g tensor. Shifts of g associated with spin–orbit perturbation by heteroatoms are well-known.[16] Moreover, oxygen hyperfine splitting can be detected in a sample of 4-¹⁷O, generated by irradiation of 6-¹⁷O, ~40% enriched,[17a] which in turn is prepared

(1) For a review, see: Borden, W. T. *React. Intermed.*, in press.
(2) Salem, L. *Pure Appl. Chem.* **1973**, *33*, 317.
(3) (a) Hund, F. "Linienspecktren und periodisches System der Elemente"; Springer-Verlag: Berlin, 1927; p 124. (b) *Z. Phys.* **1925**, *33*, 345.
(4) (a) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587. (b) Borden, W. T. *Ibid.* **1975**, *97*, 5968.
(5) Kollmar, H.; Staemmler, V. *Theor. Chim. Acta* **1978**, *48*, 223.
(6) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297.
(7) (a) For a list of references on non-Kekulé hydrocarbons, see ref. 9. See also: (b) Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969; p 232. (c) Dewar, M. J. S.; Dougherty, R. C. "The PMO Theory of Organic Chemistry"; Plenum: New York, 1973, pp 73 ff. (d) Döhnert, D.; Koutecky, J. *J. Am. Chem. Soc.* **1980**, *102*, 1789.
(8) Platz, M. S.; Burns, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 4425.
(9) Rule, M.; Matlin, A. R.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5098.

(10) MS M_r 156.0577. Calcd for $C_{11}H_8O$: 156.0575. Analysis by Dr. T. Wachs, Cornell University.
(11) House, H. O.; Paragamian, V.; Ro, R. S.; Wluka, D. J. *J. Am. Chem. Soc.* **1960**, *82*, 1452.
(12) Wasserman, E.; Hutton, R. S. *Acc. Chem. Res.* **1977**, *10*, 27 and references cited therein.
(13) By the method of Kottis and Lefebvre (Kottis, P.; Lefebvre, R. *J. Chem. Phys.* **1964**, *41*, 379) as programmed for a Wang calculator by Professor J. M. McBride, to whom we are indebted.
(14) The possibility that the diyls 3 and/or 4 may be of the σ–π type[15] rather than the all-π type assumed in our calculations cannot be ruled out at present.
(15) McBride, J. M.; Merrill, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 1723 and references cited therein.
(16) Cf. inter alia: Schneider, F.; Möbius, K.; Plato, M. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 856.

Scheme I^a
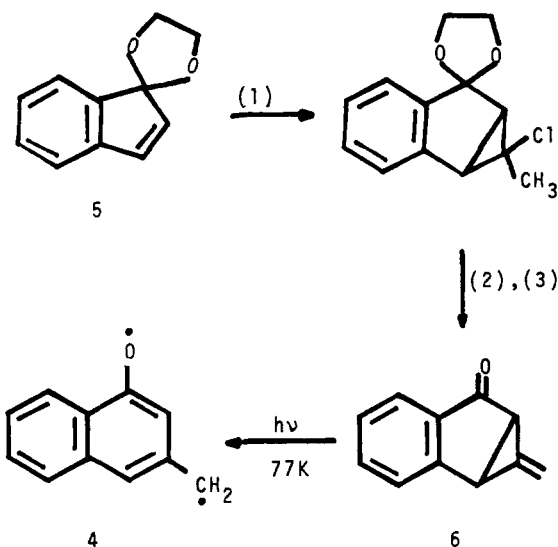
^{a} (1) CH$_3$CHCl$_2$, BuLi, −30 °C, Et$_2$O; (2) KO-*t*-Bu, Me$_2$SO, 60 °C; (3) THF, 5% H$_2$SO$_4$.
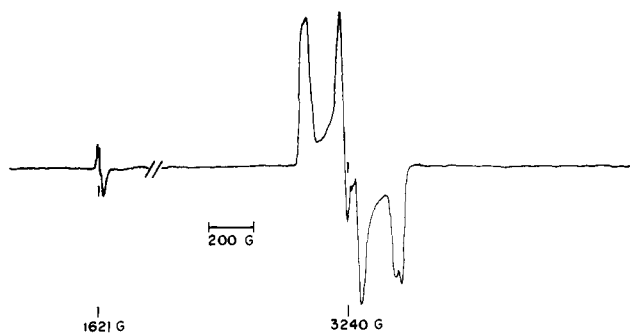

200 G

1621 G   3240 G

Figure 1. EPR spectrum of the triplet species **4** generated by irradiation of a 2-methyltetrahydrofuran matrix of enone **6** at 77 K. The small absorption near 3245 G is due to cavity background.

by hydrolysis of the corresponding ketal with H$_2$^{17}O/HCl.[17b] The details of the splitting cannot be seen in the randomly oriented sample, but increased line widths and altered line shapes, especially of the lowest- and highest-field $\Delta m_s = \pm 1$ transitions, are clearly discernible in the EPR spectrum of the labeled material (Figure 2). Similar perturbations of the extreme $\Delta m_s = \pm 1$ transitions of the monocyclic analogue **3** now also have been observed.[18]

In a polycrystalline matrix prepared by irradiation at 193 K of a frozen 0.1 M benzene solution of **6**, the EPR signal of **4** decays to about 5% of its original intensity with a rate that can be fitted to second-order kinetics. The remaining signal, which upon rescanning is seen to be identical in form with the starting spectrum, persists for a time equivalent to many additional half-lives of the second-order reaction. We tentatively interpret this behavior to mean that biradicals are generated in nonhomogeneous distribution in the matrix. Whether dimers corresponding to the second-order process can be observed on a preparative scale is not yet known.

A plot of the EPR signal intensity of **4** vs. reciprocal of absolute temperature is linear in the range 16–85 K. Below 16 K, the plot is convex, but at least part of this curvature is attributable to saturation associated with slow restoration of the Boltzmann spin distribution, as is clear from the nonlinear dependence of the signal intensity I upon the square root of the microwave power.[19] If we ignore the contribution of this effect and assume that the

Figure 2. (a) Expanded view of the high-field z transition of **4**. (b) The high-field z transition of **4**-^{17}O, 40% isotopically enriched.

curvature in the experimental intensity I vs. $1/T$ plot is due solely to thermal population of a triplet state from a hypothetical singlet ground state, we may estimate an upper limit of the energy gap between these states by matching the experimental points to a curved plot calculated from eq 1 by using varying small values

$$I = (a/T)(3[\exp(-\Delta E/RT)])/(1 + 3[\exp(-\Delta E/RT)]) \quad (1)$$

of ΔE. In eq 1, the constant a is determined empirically from the linear portion of the plot (>30 K). By this procedure, we conservatively estimate that the singlet cannot be lower in energy than the triplet by more than 0.01 kcal/mol. Accordingly, either the triplet and singlet are nearly degenerate or the triplet is the ground state.

Detailed theoretical treatment of the spin states of such systems would be valuable. In the meantime, the present and previous[8,9] empirical evidence suggests that heteroatomic analogues of non-Kékulé hydrocarbons potentially constitute a large class of molecules that have high-spin ground states, even when the heteroatom substitution lifts the degeneracy of the Hückel NBMOs.[20]

(17) (a) Analysis by mass spectrometry. (b) We thank Professor J. M. McBride for a gift of H$_2$^{17}O.

(18) We thank Mr. A. R. Matlin for this experiment.

(19) Wertz, J. E.; Bolton, J. R. "Electron Spin Resonance"; McGraw-Hill: New York, 1972; p 456.
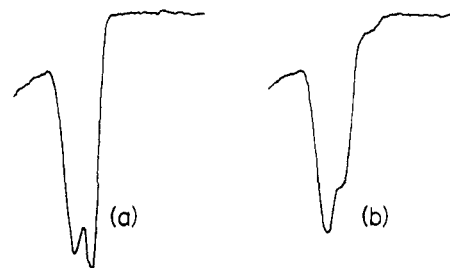
(20) In some instances (e.g., the trisiminomethanes[21]), a highly symmetrical substitution pattern may preserve a Hückel degeneracy of the partially filled HOMOs. In a formal sense, Hund's rule applies to such molecules.

(21) Quast, H.; Bieber, L.; Danen, W. C. *J. Am. Chem. Soc.* 1978, *100*, 1306.

Chirally Directed Synthesis of (−)-Methyl 5(S),6(S)-Oxido-7-hydroxyheptanoate (1), Key Intermediate for the Total Synthesis of Leukotrienes A, C, D, and E

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The levorotatory epoxy ester **1** has previously been synthesized in this laboratory and applied to the preparation of leukotriene A (**2**)[1] which is a synthetic[1,2] and biosynthetic[3] progenitor of the slow reacting substances (SRS's) leukotrienes C,[4] D,[5] and E.[6] In

(1) Corey, E. J.; Clark, D. A.; Goto, G.; Marfat, A.; Mioskowski, C.; Samuelsson, B.; Hammarström, S. *J. Am. Chem. Soc.* 1980, *102*, 1436, 3663.

(2) Corey, E. J.; Barton, A. E.; Clark, D. A. *J. Am. Chem. Soc.* 1980, *102*, 4278.

(3) Rådmark, O.; Malmsten, C.; Samuelsson, B.; Clark, D. A.; Goto, G.; Marfat, A.; Corey, E. J. *Biochem. Biophys. Res. Commun.* 1980, *92*, 954.