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NON-KEKULÉ MOLECULES DERIVED CONCEPTUALLY BY HETEROATOM-FOR-CARBON SUBSTITUTION IN ALTERNANT HYDROCARBONS

M-QUINOMETHANE AND *M*-NAPHTHOQUINOMETHANE[1]

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Abstract—Qualitative theoretical considerations suggest that substitution of a heteroatom for a C atom in an alternant hydrocarbon might result in a non-Kekulé molecule with a triplet ground state, despite the non-degeneracy of the Hückel NBMOs of the heteroatom derivative. The syntheses of 3-methylene-1-phenoxyl and 3-methylene-1-naphthoxyl are described. These compounds, biradical valence tautomers of *m*-quinomethanes, are characterized by EPR spectroscopy and are assigned triplet ground states. Optical resolution of 6-methylene-bicyclo[3.1.0]hex-3-ene-2-one, the precursor of 3-methylene-1-phenoxyl, is described. Repeated irradiation of the active ketone at 20K with intermittent warming to room temperature followed by re-isolation gives ketone of undiminished activity, which suggests that re-cyclization of (presumably achiral) 3-methylene-1-phenoxyl does not occur under these conditions.

A non-Kekulé molecule may be defined as one that contains enough atoms but not enough bonds to satisfy the standard rules of valence. Classical structural theory and practical experience teach us that such species should be elusive if not actually incapable of existence. However, the range of conditions available for experimental inquiry has recently expanded so greatly that the isolation and characterization of a number of non-Kekulé compounds have been achieved and, in a few instances, the use of these substances as synthetic reagents has been effected. With the rules of valence relaxed, it is possible to conceive of a vast new group of molecules with unique properties.

A primary task for the expansion of this field is the accumulation of a body of examples which will serve as an empirical basis for theoretical studies and for predictions of the stability and spin state of non-Kekulé compounds. The present paper describes the experimental development of a class of such molecules upon simple theoretical grounds.

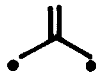
We expect a non-Kekulé molecule when (but not invariably when) a simple Hückel theoretical treatment of the π-electron system yields $2r$ ($r = 1, 2, \ldots$) incompletely occupied degenerate nonbonding molecular orbitals (NBMOs). Longuet-Higgins[2,3] has given a simple rule for the prediction of the minimum number of NBMOs (k_{min}) in the special case of alternant hydrocarbons (eqn 1),

$$k_{\min} \geq N - 2T \qquad (1)$$

where N is the number of π-electron centers, and T is the number of double bonds in the resonance structure containing the maximum number of double bonds. For most alternant hydrocarbons the lower limit of eqn 1 may be replaced by an equality, with the notable exception of $4N$ annulenes. Simple examples are benzene (**1**), trimethylenemethane (**2**), and cyclobutadiene (**3**) (Table 1).

Spin of the ground state of non-Kekulé molecules. The structures of concern here all resemble trimethylenemethane in having one broken bond and hence are unambiguously classifiable as non-Kekulé. The prediction of the spin of their ground states can be approached through detailed quantum mechanical calculation, but the working chemist also benefits from the guidance provided by more qualitative theoretical considerations. In a sense, the presently available generalizations on the subject may be thought to serve an intellectual function in the field of π-conjugated biradical and multiradical systems which corresponds to that of simple Hückel theory in conventional π-conjugated systems. The value of Hückel theory as a stimulus to experiment and as a guide to

Table 1. Predicted minimum number (k_{min}) of NBMOs from eqn (1) and calculated number (k_{calc}) from simple HMO Theory

	 1	 2	 3
$\underline{N}$	6	4	4
$\underline{T}$	3	1	2
k_{min}	0	2	0
k_{calc}	0	2	2

interpretation is widely appreciated, even though its theoretical basis is less than rigorous.[4]

The simplest method for prediction of the spin state involves the application of Hund's first rule:[5,6] of the spin states of a given electronic configuration, the one of the highest multiplicity will have the lowest energy. For the systems of concern here, this can be expressed as eqns (2) and (3),

$$S = k_{\text{calc}}/2 \qquad (2)$$

$$\text{Multiplicity} = 2S + 1 = k_{\text{calc}} + 1 \qquad (3)$$

where S is the total spin of the ground state. On this basis, π-conjugated biradicals, for example, should have triplet ground states.

However, Borden and Davidson[7] have pointed out that such biradicals (and, we presume, multiradicals) can be classified into two types, according to whether or not their Hückel NBMOs are *disjoint*, that is, are confinable so that they have no atoms in common. If they can be so confined, the wave function contains no high energy terms that correspond to the simultaneous occupation of the same atomic orbital (AO). Consequently, the electron repulsion effect, which is a major cause of the singlet–triplet energy splitting in non-disjoint systems, is relieved. The lowest singlet and triplet states of a disjoint system are nearly degenerate at the SCF level of calculation, and in the actual molecule, Hund's rule *may* be violated.[8] Using the simple procedures given,[7] it is easy to verify the classifications, for example, of trimethylenemethane (**2**) and *m*-quinomethane (**4**) as nondisjoint, and of tetramethyleneethane (**5**) and cyclobutadiene (**3**) as disjoint.

It is of historical interest that E. Hückel[9] also recognized the role of electron repulsion effects on the magnitude of the singlet–triplet splitting. Although he did not generalize his deductions, he suggested that the singlet and triplet states of the hydrocarbon (**6**) should be nearly degenerate. Compound **6** would be classified as a disjoint system by the Borden–Davidson scheme.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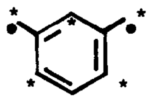
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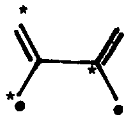
non-disjoint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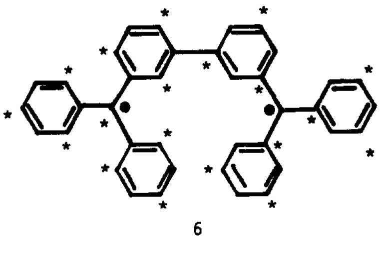
disjoint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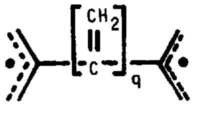
A. Ovchinnikov[10] has developed a different and bolder rule for alternant hydrocarbons, from which a more definite prediction about the disjoint systems can be made. Using the framework of valence bond theory, and expressing the exchange integral in terms of the parameters of a Pariser–Parr–Pople Hamiltonian, he has derived the total spin (S) of the ground state of any alternant hydrocarbon in the form of eqn (4).

$$S = \frac{|n^* - n|}{2}. \qquad (4)$$

The terms n^* and n refer to the number of starred and unstarred positions in the π-system. It is of special interest in the context of the work to be reported here that Ovchinnikov explicitly states that eqn (4) should hold even in heteroatom-substituted cases. The application of the Ovchinnikov rule immediately predicts that the ground states of the non-disjoint systems **2** and **4** each should be triplet ($S = 1$), whereas those of the disjoint ones **5** and **3** should be singlet ($S = 0$).

It has been demonstrated that although a biradical system is disjoint whenever $n^* = n$, the converse is not true, that is, $n^* = n$ is not a necessary property of disjoint alternant systems.[7] Therefore, not every disjoint compound is predicted by eqn (4) to have a singlet ground state. An illustrative example is provided by the series of compounds derived from tetramethyleneethane (**5**) by insertion of $q = 1, 2, 3, \ldots$ etc. $CH_2 = C$ units into the central C–C bond. Although all such compounds, like the parent (**5**, $q = 0$), are disjoint, eqn (4) predicts $S = 0$ ($|n^* - n| = 0$) when q id even, but $S = 1$ when q is odd ($|n^* = n| = 2$). These relationships contain the elements of a significant future test of theory.



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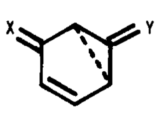
Although much of the framework for predicting the spin states of biradicals is based on the theoretical properties of hydrocarbons, the range of application of these ideas clearly would be greatly increased if the effect of heteroatom-for-carbon substitution could be predicted. Practical considerations often might make the heteroatom system more readily accessible by synthesis, and some useful theoretical insights might be provided by treating such molecules as perturbed hydrocarbons.

In strict terms, neither the Longuet-Higgins[2] NBMO-counting method nor the Borden–Davidson[7] classification according to disjoint character makes such predictions. However, the Ovchinnikov approach suggests that predictions for the hydrocarbon should hold for the heteroatom derivative.[10] We have been stimulated by this idea because it does not seem to be derivable by intuitive extrapolation from simple Hückel theory. The degeneracy of the NBMOs of an alternant biradical in general will be split by unsymmetrical[11] heteratom substitution, and although qualitative arguments might suggest that a more sophisticated calculation would tend to reduce the splitting, there is no obvious way to predict the spin of the ground state in such a case without thorough numerical investigation.

Synthesis and EPR spectroscopy of the m-*quinomethane and* m-*naphthoquinomethane biradicals.* The structure *m*-quinone (**7a**) and its derivatives *m*-quinomethane (**7b, c**) and *m*-quinodimethane (**7d**)[12] each can be thought of as the symbol for a pair of valency tautomers: an ordinary covalent molecule (**8**) and a biradical (**9**). In these systems, the relief of ring-strain and the liberation of aromatic resonance in **9** pay for the energy required to break a covalent bond in **8**. Table 2 shows that in three of the four comparisons, bond-addivity data predict that **9** actually should be more stable than **8**. These calculations are quite crude and could be in error by several kcal/mol, but they suffice to show at least that the non-Kekulé structure is not expected to be much higher in energy than the covalent one.



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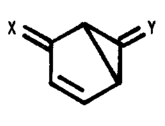

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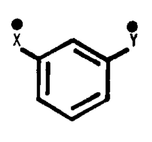
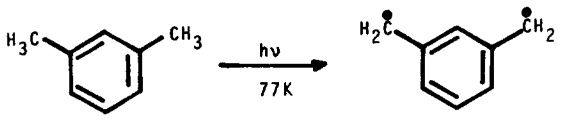


9

a: X = Y = O
b: X = O; Y = CH_2
c: X = CH_2; Y = O
d: X = Y = CH_2
e: X = Y = CPh_2

An early synthesis of a *m*-quinonoid compound (**9e**) was provided by Schlenk and Brauns.[14a] The triplet state of this biradical can be observed by EPR spectroscopy.[14b,c] These experiments, although significant in their own right, pertain to a substance (**9e**) in which the phenyl groups strongly stabilize the biradical form. It is therefore questionable whether the observed properties serve as a model for the unperturbed system.

The first experimental report of a simple *m*-quinonoid compound was that of Migirdicyan and Baudet.[14c] These authors irradiated *m*-xylene at 77K and obtained a preparation, the optical fluorescence and excitation spectra of which they interpreted as indicating the presence (among other chromophores) of *m*-quinodimethane (*m*-xylylene, **9d**). They also concluded that the observed carrier of the optical spectra was a triplet molecule. No direct evidence of the spin state, for example, by electron paramagnetic resonance (EPR) spectroscopy was reported.



9d

In view of the known[14d] photochemical conversion of toluene to benzyl radical, the formation of **9d** under the reported [14c] conditions is not implausible. However, for the experimental spectroscopic determination of the lowest spin state, EPR is the most reliable method available.[15] Our first objectives, therefore, are to develop a directed synthesis of a *m*-quinonoid biradical and, if possible, to characterize it by EPR spectroscopy.

Scheme 1 outlines a synthesis of 6-methylenebicyclo[3.1.0]hex-3-en-2-one (**8b**), a covalent tautomer of *m*-quinomethane, from cyclopentenone ethylene ketal (**10**). The enone **8d** can be purified by gas chromatography (GC) and is obtained as a colorless liquid which is reasonably stable thermally.

Irradiation at ⩾310 nm of **8b** in glassy matrices in 2-methyltetrahydrofuran at 77K causes a bright yellow color. If the irradiation is carried out in the microwave cavity of the EPR spectrometer, a weak spectrum appears which can be ascribed to that of a randomly oriented triplet molecule. The signal intensity can be

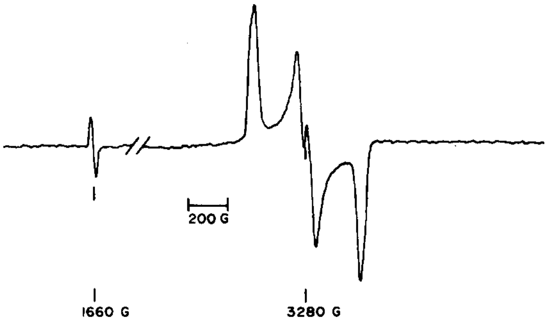


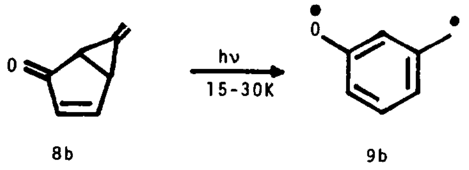
Fig. 1. EPR spectrum of the triplet species **9b** generated by irradiation of a 2-methyltetrahydrofuran matrix of the enone **8b** at 15–30K.

Table 2. Relative energies of covalent (**8**) and biradical (**9**) forms of *m*-quinonoid valency tautomers[a]

Compound	ΔH_f (8)	ΔH_f (9)	$\Delta H_f(9) - \Delta H_f(8)$
8a/9a	–4.4	5.8	10.2
8b/9b	44.1	39.9	–4.2
8c/9c	41.4	39.9	–1.5
8d/9d	90.2	70.1	–20.1

[a] The ΔH_f values are calculated using the group equivalents of Benson[13] and the assumption that the strain energy in the covalent form **8** is at least 45 kcal/mol. No correction for the spin state is included. The strain energy of ~45 kcal/mol is estimated by analogy to other systems. *Cf.* J. F. Liebman and A. Greenberg, *Strained Organic Molecules*. Academic Press, New York (1978).

increased by incorporation of benzophenone (presumably acting as a sensitizer) into the sample before freezing it. More efficient production of the signal, even in the absence of a sensitizer, is achieved by irradiation at cryogenic temperature (15-30K, Fig. 1). Curie plots (EPR signal intensity vs $1/T$) for this species are difficult to obtain because the signal disappears irreversibly at above 40K and saturation effects are serious at low temperatures. The narrow temperature range precludes a firm assignment of the ground state multiplicity, but by analogy to the benzo derivative to be described, it probably is triplet.



Several independent pieces of evidence support the assignment of the structure 3-methylenephenoxyl (**9b**) to the carrier of the EPR spectrum. The signal does not seem to be caused by an impurity or a radical-pair, since a sample recovered from spectroscopy and re-purified gives the same spectrum and since the same spectrum is generated in three different matrices: 2-methyltetrahydrofuran, 3-methylpentane, and benzene.

Moreover, the carrier of the signal is clearly a molecule with significant spin-density on oxygen. A fit of the spectrum to a spin Hamiltonian (see below) can be achieved only by the use of an anisotropic g-tensor. g-Shifts associated with spin-orbit perturbation by heteroatoms are well known.[16a] Direct evidence for spin density on oxygen is provided by the spectrum of a sample enriched with ^{17}O (Fig. 2). The hyperfine interaction of the ^{17}O nucleus ($I = 5/2$) with the electron spins would be expected to cause additional lines in the EPR spectrum. Although the individual splittings cannot be seen in the randomly oriented sample, definite changes in line-shape can be observed.

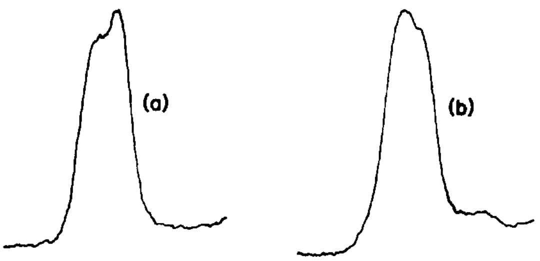


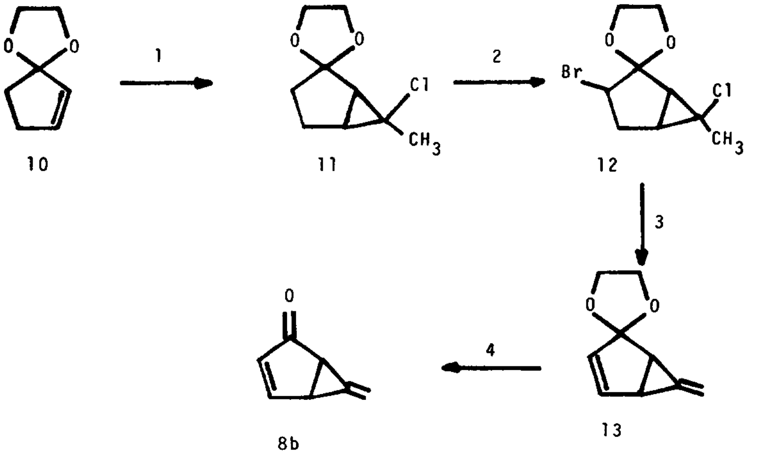
Fig. 2. (a) Expanded view of the low-field $\Delta M_s = \pm 1$-transition of **9b**. (b) The low-field $\Delta M_s = \pm 1$-transition of **9b**-^{17}O, 30% isotopically enriched.

The zero-field splitting (ZFS) parameters (in cm^{-1}), $|D| = 0.0266 \pm 0.0002$, and $|E| = 0.0074 \pm 0.0002$, obtained by fitting the spectrum to a spin Hamiltonian,[16b] are appropriate for the structure **9b**. Although an accurate quantum mechanical calculation of ZFS can be achieved by *ab initio* methods only by the use of a large basis set and configuration interaction,[17] semi-empirical methods can be used to obtain reasonable agreement between theory and experiment. For example, the point-charge approximation of McWeeny[18] has been combined with various parameterization techniques[14b,19] for this purpose. It should be noted that small values of $|E|$ are difficult to calculate accurately by the available methods, so that only $|D|$ values are useful for comparison with experimental data in these systems.

One approach to the calculation of $|D|$ is to calibrate McWeeny's approximation using experimental values of known biradicals with structures similar to those of the present non-Kekulé compounds. Spin-orbit contributions to the ZFS are assumed to be negligibly small in the systems listed in Table 3, and the value of $|D|$ is based solely upon the spin–spin dipolar interaction, which is described by the Hamiltonian (eqn 5), where $\hat{S}$ is

$$\mathcal{H}_{SS} = \hat{S} \cdot D \cdot \hat{S} \qquad (5)$$

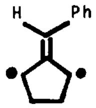
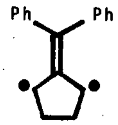
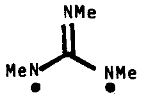
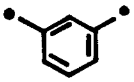
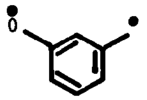
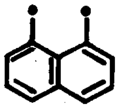
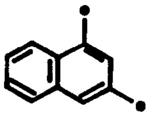
the total spin operator and **D** is a traceless second-rank



Scheme 1[a].

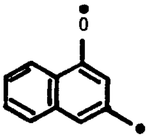
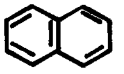
[a]Methods: (1) CH_3CHCl_2, BuLi, −30°C, pentane, following a general procedure of S. Arora and P. Binger, *Synthesis* 1974, 801; (2) Br_2, Et_2O, 0°, following a general procedure of E. W. Garbisch, *J. Org. Chem.* **30**, 2109, 1965; (3) 4 equiv of KOt-Bu, Me_2SO, 60°C; (4) Et_2O, 5% H_2SO_4.

Table 3. Experimental and calculated values of the ZFS parameter $|D|$ for several organic triplet species

Entry	Cpd.	$\lvert D\rvert/hc$, cm^{-1} Exptl.	Calc.
1.		0.0248[a]	0.052[m]; 0.0522[n]
2.		.0256[b]	.0456[e]; .0470[p]
3.		.0196[b]	.042[m]
4.		.0180[b]	.0389[m]
5.		.012[c]	.049[m]; .0497[o]
6.		.0204[d]	.049[m]; .0497[o]
7.		.033[e]	.0677[o]; .0767[n]
8.			.032[m]; .0337[p]; .0337[q]
9.		.0266[f,g]	.0542[o]; .0567[p]
10.		.0218[h]	.040[m]; .0443[o]
11.			.0320[o]

(Cont.)

Table 3. (*Contd*)

Entry	Cpd.	$|D|/hc$, cm^{-1} Exptl.	$|D|/hc$, cm^{-1} Calc.
12.		.0204[f,i]	.0438[o]
13.		.084[i]	.0724[p]; .0776[q]
14.		.1581[k]	.120[m]
15.		.1003[l]	.093[r]; .067[m]

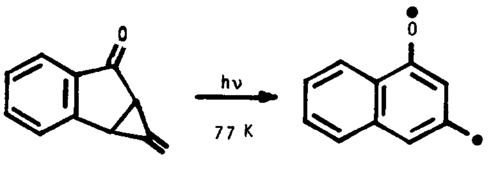
[a]O. Claesson, A. Lund, T. Gillbro, T. Ichikawa, O. Edlund and H. Yoshida, *J. Chem. Phys.* **72**, 1463 (1980); *cf* R. J. Baseman, D. W. Pratt, M. Chow, P. Dowd, *J. Am. Chem. Soc.* **98**, 5726 (1976); P. Dowd, *Ibid.* **88**, 2587 (1966); P. Dowd, M. Chow, *Ibid.* **99**, 6438 (1977); [b]M. S. Platz, J. M. McBride, R. D. Little, J. J. Harrison, A. Shaw, S. E. Potter and J. A. Berson, *Ibid.* **98**, 5725 (1976); [c]P. Dowd, *Ibid.* **92**, 1066 (1970); [d]W. R. Roth and G. Erker, *Angew. Chem* Intl. Ed. Engl. **12**, 503 (1973); [e]Ref. 11*b*; [f]this work; [g]Ref. 1*a*; [h]R. Pagni, M. N. Burnett and J. R. Dodd, *J. Am. Chem. Soc.* **99**, 1972 (1977); M. S. Platz, *Ibid.* **101**, 3398 (1979); *cf* also J. F. Muller, D. Muller, H. Dewey and J. Michl, *Ibid.* **100**, 1629 (1978) for a related structure; [i]Ref. 1*b*; [j]S. L. Buchwalter and G. L. Closs, *J. Am. Chem. Soc.* **101**, 4688 (1979); [k]M. S. de Groot, I. A. Hesselmann and J. H. van der Waals, *Mol. Phys.* **16**, 45 (1969); [l]C. A. Hutchison, Jr. and B. W. Mangum, *J. Chem. Phys.* **29**, 952 (1958); **34**, 908 (1961); [m]Calculation based on HMO wave functions; [n]Calculation based on CNDO closed-shell singlet wave functions; [o] Calculation based on CNDO triplet wave-functions; [p]Calculation based on INDO triplet wave-functions; [q]Calculation based on INDO closed-shell singlet wave-functions. [r]Calculation based on πSCF-CI wave functions with singly and doubly excited configurations: J. H. van der Waals; G. ter Maten, *Mol. Phys.* **8**, 301 (1964).

tensor. When $\mathbf{D}$ is diagonalized to $^d\mathbf{D}$, the diagonal elements $D_{II}(I = X, Y, Z)$ are the relative energies of the three triplet sublevels.[15]

Table 3 gives the results of calculations of $|D|$ values for a number of biradicals and compares these with experimental data. Although for the last three entries (13–15), the values calculated using single determinant wave functions match the experimental ones to within 10–30%, the theoretical predictions in the remaining ten examples uniformly overestimate the value of $|D|$ by about a factor of two. Note that for the heteratom cases (7, 9, 12), the calculations assume a π,π-biradical structure, although a σ,π-biradical assignment[20a] to entries 9 and 12 (see below) cannot be rigorously excluded on the basis of the experimental facts so far available.

Confidence in the identification of 3-methylenephenoxyl (**9b**) as the EPR-active species observed in the irradiation of the enone **8b** is strengthened by the synthesis and photolysis of the benzo derivative **14** (Scheme II). The synthetic steps are similar to those of Scheme I, except that the oxidation state of the starting material, indenone ketal (**15**), already is appropriate, and the bromination-dehydrobromination sequence of Scheme I is not required.

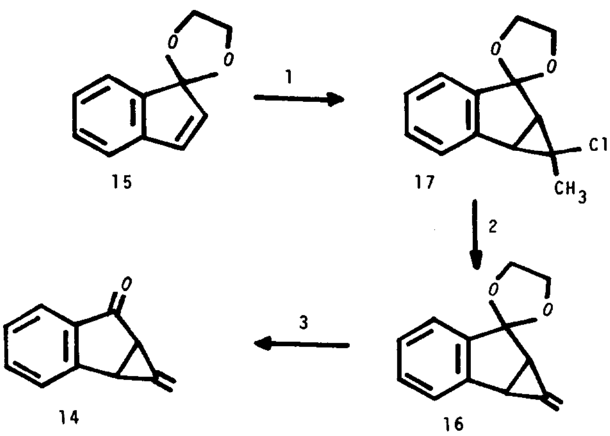
Irradiation (>310 nm) of the benzo enone **14** in a rigid matrix at 77K gives a bright orange preparation with the EPR spectrum[1b] of a randomly oriented triplet species. Analysis of the spectrum gives the ZFS parameters (in cm^{-1}) $|D|/hc = 0.0204 \pm 0.0002$, $|E|/hc = 0.0052 \pm 0.0004$ which we assign to the structure 3-methylene-1-naphthoxyl, **18**. It is reasonable that benzo annelation (**9b** → **18**) should decrease the $|D|$-value (compare **9b**, $|D|/hc = 0.0266$ cm^{-1}). D is a measure of the average separation of the unpaired electrons. The calculated $|D|$-value (see Table 3, entry 12), when scaled by the empirical factor of 0.5, agrees well with the observed value.



14 18

Hydrolysis of the benzo ketal **16** with $H_2{}^{17}O$ gives ketone **14**-^{17}O, 40% enriched, which upon irradiation at low temperature gives an EPR spectrum again showing line-shape changes as compared to that of its unlabeled counterpart.

The temperature-dependent behavior of the EPR spectrum of **18** in 2-methyltetrahydrofuran is reversible between 15 and 85K, a much larger range than could be

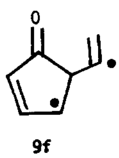


Scheme 2. Methods: (i) CH_3CHCl_2, tBuLi; (2) KOt-Bu, DMSO; (3) THF, 5% H_2SO_4.

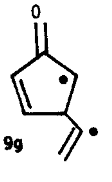
observed for the monocyclic biradical **9b**. The Curie plot is linear in this region. Below 15K, some convexity is observed, but it is likely that most if not all of the curvature is attributable to saturation effects. We estimate that any singlet species cannot be lower in energy than the triplet by more than about 0.01 kcal/mole. Thus, either the two states are almost exactly degenerate or, more plausibly, the triplet is the ground state.

Again, the line-shape is independent of temperature, even up to $-80°$.

A referee has asked whether the carrier of the EPR signal from **8b** might be a biradical **9f** or **9g** resulting from cleavage of the C_1–C_5 bond. Calculation by the above method of the *D*-value for **9f**, which should be the more stable of the **9f**-**9g** pair, suggests that *D* for this species would be at least 50% greater than that observed. We do not consider this sufficient to rule out **9f**. However, the calculations indicate that geometric inversion of the vinyl radical center of **9f** would be accompanied by a substantial change in *D*. Since the inversion rate for vinyl radical[20b] changes from fast to slow on the EPR timescale as the temperature is lowered through the range corresponding to that of the present measurements, a perceptible change in the spectrum might reasonably have been anticipated, but no such changes are observed for the species derived from **8b**. Finally, it is not obvious why the photolysis should cleave a strong bond to form **9f** or **9g** and avoid cleaving a weak one to form the aromatically stabilized species **9b**. Chemical evidence that the bridge bond breaks efficiently in the solution photochemistry of **8b** is given in the following section. Although no single piece of evidence we have rules out **9f** or **9g**, the probability that these species can account for the observations does not seem great. One further experimental distinction between the vinyl radicals **9f**/**9g** and the delocalized system **9b** could be made by observation of the hyperfine coupling effect of ^{13}C labeling at C_6 and (separately) C_7 of **8b**.

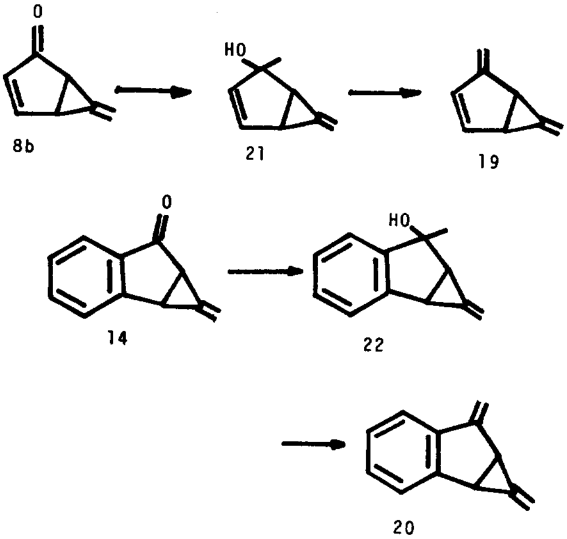


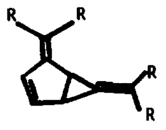
9f



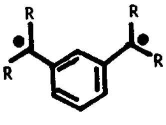
9g

Reactions of 6-methylene bicyclo[3.1.0]*hex-3-ene-2-one* (**8d**) *and its benzo analog* (**14**). Attempts to prepare the hydrocarbon analogs **19** and **20**, which are precursors of *m*-quinodimethane and *m*-naphthoquinodimethane, from the ketones **8b** and **14**, respectively, have been unsuccessful. Both ketones give tertiary alcohols (**21** and **22**) with methyllithium, but attempts to dehydrate these give rise to ill-defined, apparently polymeric products. Similar materials seem to be formed from attempted Wittig-type methylenations of **8b** or **14**. The reaction mixtures give no evidence of the formation of *m*-cyclophane products (e.g. **23**), which might have been expected from dimerization of the *m*-quinodimethane. If **19** is

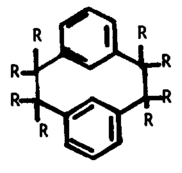




19: R = H
24: R = Me



8b

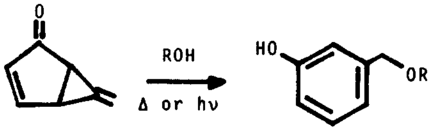


23: R = H
25: R = Me

formed at all in these reactions (which of course remains to be demonstrated), its behavior seems to be quite different from that of the tetramethyl analog **24**. Although not observed directly, the latter hydrocarbon apparently is among the products of the reaction of dimethylvinylidene with 6,6-dimethylfulvene and, under the conditions, gives the *m*-cyclophane **25** before it can be isolated.[21]

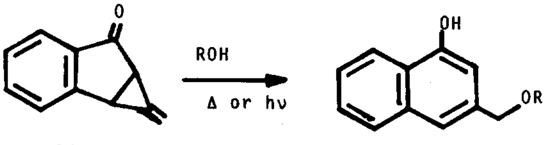
The ketone **8b** is thermally stable up to at least 100°. It can be purified by gas chromatography, and it can be recovered unchanged from boiling benzene. Pyrolysis at 150° or photolysis at 0° in *p*-cymene convert **8b** to intractable materials.

Both ketones **8b** and **14** react smoothly with alcohols under thermal or photolytic conditions. Heating in ethylene glycol or irradiation in methanol (at 0°) give the *m*-hydroxybenzyl ethers, **26** and **27**, or 1-hydroxy-3-naphthyl ethers, **28** and **29**, in high yield. It is tempting to speculate that these reactions may involve the singlet biradicals **9b** and **18**, or the zwitterions **30** and **31**, or perhaps their protonated counterparts, **32** and **33**.



8b

26: R = CH_2CH_2OH
27: R = Me



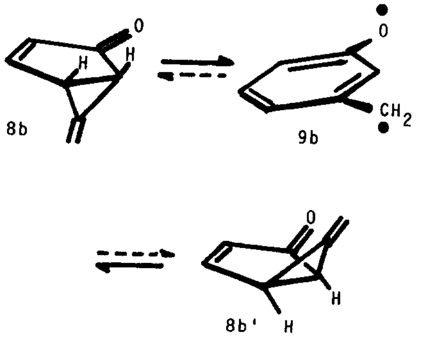
14

28: R = CH_2CH_2OH
29: R = Me

30: R = ⊖
32: R = H

31: R = ⊖
33: R = H

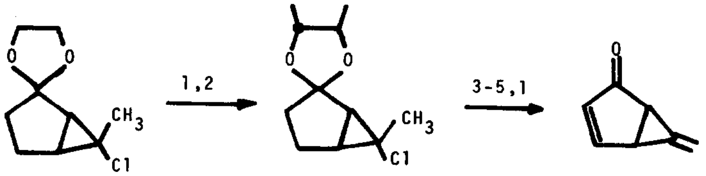
Table 2 shows that the energy difference between the covalent and biradicaloid forms of the valency tautomeric pair **8b**/**9b** is only 4.2 kcal/mol. This suggests that, unless there is a large singlet–triplet splitting in the biradical, thermal or photochemical reversible interconversion of the valency tautomers might be effected. Since ketone **8b** is chiral but the biradical **9b**, the zwitterion **30**, and the cation **32** all are achiral, it might be possible to observe such a reaction by following the decline in optical rotation of an optically active sample of **8b**.



Optically active **8b** (configuration unknown) can be prepared by the procedure shown in Scheme III. The ethylene ketal **11** (Scheme I), obtained as 9 : 1 mixture of C-6 epimers, is deketalized and the resulting ketone re-ketalized with optically pure (−)-2,3-butanediol.[22] Preparative GC of the four-component mixture of diastereomers thus formed permits the concentration of one isomer, which upon bromination, dehydrohalogenation, and deketalization gives optically active enone **8b**, $[\alpha]_{365}$ − 2340 ± 37° (cyclohexane).

Irradiation of (−)-**8b** in a 2-methyltetrahydrofuran matrix at 20K in the EPR spectrometer cavity gives rise to the characteristic triplet spectrum of **9b**, which reaches its maximum intensity within 90s. The cycle is repeated several times by warming the sample to room temperature, re-freezing, and re-irradiation. Isolation by GC of the enone **8b** remaining after 2, 3 and 10 cycles gives material with, respectively, $[\alpha]_{365}$ − 2290 ± 290°, −2270 ± 39°, and −2700 ± 380°. These values do not differ significantly from those of the starting enone.

The apparent absence of racemization of **8b** in this sequence of experiments suggests that thermal recyclization of the biradical **9b** does not occur. We have considered an alternative explanation, namely that only a small fraction of the **8b** is converted to **9b** in each photolytic cycle. Although readily detectable by the extremely sensitive EPR method, the small amount of **9b** formed could recyclize, but the effect on the optical rotation of recovered **8b** might fall below the limit of preception. The observation that the EPR signal intensity regenerated after 9 cycles is still about 80% of that produced in the first cycle seems to support this hypothesis. On the other hand, some evidence that a photochemical transformation occurs is provided by NMR analysis of the crude reaction mixture obtained when the solvent is evaporated after repeated irradiation-warm-up cycles. The presence of substantial amounts of (so far unidentified) products is evident. Moreover a direct



11

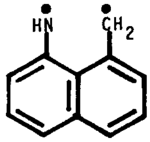
(−)-8b

Scheme 3. Methods: (1) 5% H_2SO_4, THF; (2) (−)-2,3-butanediol, TsOH; (3) GC sepn.; (4) Br_2; (5) t-BuOK, DMSO.

determination ("spin count") of the absolute yield of biradicals shows that about 6% of the starting enone **8b** is converted to **9b** in one 90s irradiation. The repeated cycles thus should have produced an easily detectable decline in optical rotation in the recovered **8b**. Unless one is willing to argue in favor of the hypothesis that the triplet biradical (and/or its environment) is chiral and preserves all of the original optical purity of the ketone, it seems difficult to avoid the conclusion that re-cyclization to **8b** does not occur under these conditions.

CONCLUSIONS

The demonstration of low-lying triplet states for the biradicals **9b** and **18** parallels observations by Platz and Burns[23] in the case of 8-imino-1-naphthomethyl, **34**, which has been assigned a triplet ground state. These findings suggest that heteroatom-for-carbon substitution in alternant non-Kekulé hydrocarbons may well provide a rich source of high-spin organic molecules, even when the substitution splits the energies of the hydrocarbon's Hückel NBMOs.



34

EXPERIMENTAL

EPR measurements used a Varian E-9 spectrometer operating at a microwave frequency of 9.118 GHz (for **18**) and 9.064 GHz (for **9b**). "Spin counts" were carried out by the previously described method,[24] using diphenylpicryl hydrazide as the standard. NMR spectra at 90 MHz were taken with either the Perkin–Elmer R-32 or Jeol FX-90Q instruments; at 270 MHz, we used the Bruker HX-270 system. Mass spectra (MS) were recorded on the Hitachi–Perkin–Elmer RMU-6 single focussing instrument. Exact masses were obtained with the AEI-MS-9 instrument by Dr. Walter McMurray and Mr. Craig Whitehouse of the Division of Health Physical Sciences of Yale University, Mr. Marvin Thompson, University of Connecticut, or Dr. Tim Wachs, Cornell University. Elemental analyses were performed by Dr. R. C. Rittner of Olin Corporation, New Haven, Connecticut.

Scheme I

6-*Methyl-6-chlorobicyclo*[3.1.0]*hex-2-one ethylene ketal* (**11**). Cyclopentenoneethylene ketal (10 grams/79.4 mmol) and 1-1, dichloroethane (13.4 ml/159 mmol) were charged into a flame-dried 250 mL flask equipped with a mechanical stirrer, N_2 inlet, addition funnel, and low temp thermometer. A small quantity of dry pentane (~15 mL) was added and the mixture was vigorously stirred at −40°. n-BuLi 2.1 M (76 mL, 160 mmol) in hexanes was slowly added via the addition funnel, while the temp was maintained between −40° and −30°. After the addition was complete (~40 min) the mixture was stirred for 10 min at −20° and then quenched with H_2O. The mixture was taken up in 150 mL ether and washed 2 × 75 mL with H_2O, and 1 × 75 mL with brine. The organic phase was dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo* giving 13.35 g (90%) of **11** as a mixture of C-6 epimers, b.p. 60°/0.2 torr.

H NMR (90 mHz, $CDCl_3$): δ3.95 (br s, 4H), 2.2–1.5 (m, 6H), 1.58 (s, 3H); ^{13}C NMR (20 MHz, $CDCl_3$) major isomer: 118.2 (s), 64.8 (t), 63.25 (t), 48.96 (s), 34.5 (t), 31.7 (d), 28.7 (q), 23.2 (t); minor isomer: 118.2 (?, weak signal), 63.58 (t), 63.25 (t, superimposed on major peak) 38.07 (d), 35.88 (t), 32.81 (d), 28.72 (s, superimposed on major peak), 22.57 (d), 19.15 (q); MS (*m/e*): 188 (M), 190 (M + 2), 153, 126, 86 (base peak).

That two C_6 epimers are present is barely visible in the proton NMR at 90 mHz, but is clearly revealed in the ^{13}C NMR as 9:1 mixture.

6-*Methylenebicyclo*[3.1.0]*hex-2-one-3-ene ethylene ketal* (**13**). In a 500 mL flask ketal **11** (15 g/80 mmol) was dissolved in 300 mL dry ether and cooled to 0°. Br_2 (4.25 mL/80 mmol) was slowly dripped in via a dropping funnel, while the soln was stirred magnetically. The soln gradually acquired an orange hue. After the addition was complete the reaction was stirred at room temp for 5 min and then poured into 100 mL ethylene glycol containing K_2CO_3. About 150 mL H_2O was added, and the layers were separated. The organic layer was washed with 2 × 100 mL H_2O and 1 × 75 mL brine. The organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a dark oil. This was immediately dissolved in 50 mL dry dimethyl sulfoxide and added to a soln containing t-BuOK (31.4 g/280 mmol) dissolved in 250 mL dry DMSO at 0°. The soln was stirred mechanically and heated to 70° for 90 m under N_2. (Care should be taken not to exceed 70°. The product is thermally labile and can undergo a vinylcyclopropane rearrangement.) The reaction was cooled to 0° and quenched with 250 mL water. This mixture was repeatedly extracted with pentane (5 × 100 mL). The combined pentane extracts were washed with 2 × 100 mL H_2O and 1 × 100 brine. The organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo* to give 4.3 g (50% from **11**) of the unsaturated ketal **13**.

H NMR (90 MHz benzene-d_6): δ 5.88 (d × d, 1H), 5.4, m (1H), 5.2 (t), (1H), 3.56 (d), (4H), 2.2 (m, 2H); ^{13}C NMR (22 MHz, benzene-d_6): δ 140.4 (s), 120.4 (s), 136.1 (d), 129.9 (d), 99.95 (t), 65.2 (t), 64.7 (t), 26.35 (d), 25.92 (d); MS (*m/e*): 151 (M + 1), 150 (M), 149, 106, 105, 94, 78 (base peak), 77. (Found: C, 71.80; H, 6.51. Calcd. for $C_9H_{10}O_2$: C, 72.02; H, 6.66%).

6-*Methylenebicyclo*[3.1.0]*hex-3-ene-2-one* (**8b**). A soln of **13** (3.5 g) in 70 mL diethyl ether was treated with 25 mL 5% H_2SO_4, and the mixture was stirred at room temp for 30 min. The organic layer was separated, washed successively with $NaHCO_3$ aq and brine, dried over Na_2SO_4, and concentrated to give 2.1 g (85% crude yield) of **8b**. The product was purified by elution with diethyl ether from a column of Fluorisil and then by preparative GC on a 5-ft × $\frac{1}{4}$-in 20% SE-30 column (65°, injector and detector at 100°). The pure substance emerged from the column with a retention time of about 20 min.

^1H NMR (270 MHz): δ 7.64 (d × d, 1H, J = 2.199, 5.133, β-hydrogen of enone), 5.76 (d, 1H, J = 5.133, α-hydrogen of enone), 5.27 (s, 2H, terminal CH_2), 3.04 (m, 1H, J = 2.199, bridgehead methine), 2.76 (m, 1H, bridghead methine). ^{13}C NMR (20 MHz): δ 27.46 (d), 30.03 (d), 99.62 (t), 128.92 (d), 145.28 (s), 160.20 (d), 204.00 (s). IR (cm^{-1}): 3100–2800, 1700, 1556. UV in acetonitrile (nm): 335, 250. (Found: C 79.23, H, 5.74. calcd, for C_7H_6O: C 79.23, H 5.70%).

Scheme II

3, 4-*Benzo-6-chloro-6-methylbicyclo* [3.1.0] *hex-3-ene-2-one ethylene ketal* (**17**). A dry 50 mL round-bottom flask fitted with a mechanical stirrer and low temp thermometer was flushed with N_2 and to it was added 2.58 g (148 mm) indenone ketal,[25] 4 g CH_3CHCl_2 (408 mm), and a small amount of ether as a solvent. The mixture was cooled to −35° and n-BuLi (16 3 μl, 2.5 M in hexane, 408 mm) was added dropwise over 1 hr with the mixture maintained between −30° and −40°. The soln was stirred at this temp for an additional 30 min, after which it was allowed to warm to room temp and quenched with H_2O. The soln was extracted 3 times with Et_2O, the extract was dried over $MgSO_4$ and the solvent was removed *in vacuo* to yield 2.6 g (75%) **17** as a mixture of isomers. The isomers were separated by column chromatography on silica gel using CH_2Cl_2 solvent.

Isomer 1, m.p. 96–97.5°. ^1H NMR ($CDCl_3$, 90 MHz): δ 7.28 (br, s, 4H), 4.1–4.3 (m, 4H), 2.70 (d, 1H, J = 6 Hz), 1.98 (d, 1H, J = 6 Hz), 1.72 (s, 3H); MS (*m/e*, same for both isomers): 238 (6.9), 236 (21.7), 201 (14.5), 174 (11.5), 173 (100), 128 (74.6), 102 (17.5).

Isomer 2, m.p. 94–95.5°. ^1H NMR ($CDCl_3$, 90 MHz): δ 7.28 (br, s, 4H), 4.1–4.2 (m, 4H), 2.98 (d, 1H, J = 7 Hz), 2.32 (d, 1H, J = 7 Hz), 1.29 (s, 3H).

3,4-*Benzo-6-methylenebicyclo*[3.1.0]*hex-3-ene-2-one ethylene ketal* (**16**). Compound **17** (3.47 g, 14.7 mm) dissolved in dry DMSO was added to a suspension of t-BuOK (3.3 g, 29.4 mm) in DMSO under N_2 at 60°. The mixture immediately turned dark and was stirred for 1½ hr. The soln was diluted with H_2O and continuously extracted with pentane overnight. The solvent was removed *in vacuo* to yield 2.1 g (70%) crude **16**. This material could be crystallized from pentane/ether, m.p. 64–65°. ^{1}H NMR ($CDCl_3$, 60 MHz): δ 7.26 (br, s, 4H), 5.32 (m, 2H), 4.20 (br, s, 4H), 3.06 (m, 1H), 2.53 (m, 1H); MS (*m/e*): 200 (51.6), 156 (8.8), 155 (15.8), 128 (100), 102 (15.7).

3,4-*Benzo-6-methylenebicyclo*[3.1.0]*hex-3-ene-2-one* (**14**). To a soln of **16** dissolved in THF was added 5% H_2SO_4. The mixture was stirred for 90 min at room temp, after which it was extracted with ether. The organic layer was washed with H_2O and brine and dried over $MgSO_4$. The solvent was removed *in vacuo* to yield **14** (95%). This material could be purified by sublimation, m.p. 46–47°.

^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.26–7.70 (m, 4H), 5.33 (m, 2H), 3.40 (m, 1H), 3.10 (m, 1H); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 26.0, 32.6, 101.1, 124.5, 124.9, 127.1, 133.5, 133.9, 142.7, 152.0, 199.4; MS (*m/e*): 156 (16.2), 128 (100), 102 (18.7); IR (cm^{-1}, $CDCl_3$): 3076.7, 1702.7, 1611.1; MS M_r 156.0577. Calcd. for $C_{11}H_8O$: 156.0575; UV (nm, ϵ, MeOH): 299 (3230), 255 (12,000), sloping shoulders at ~327 (708), ~341 (465).

(m-*Hydroxybenzyl*) *methyl ether* (**27**)

(a) From **8b**. A sample **8b** (30 mg) was dissolved in 10 mL abs MeOH and was photolyzed in a Pyrex test tube at 0° with 350 nm light. After 30 min, the photolysis was stopped and the solvent was removed under reduced pressure. NMR analysis of the residue indicates the produce to be (*m*-hydroxybenzyl) methyl ether, **27**.

^{1}H NMR (90 MHz): δ 7.3–7.0 (m, 1H), 6.95–6.55 (m, 3H), 5.65 (bs, 1H, OH), 4.39 (s, 2H–$C\underline{H}_2O$, 3.35 (s, 3H, $OC\underline{H}_3$).

(b) *From* m-*Hydroxybenzyl alcohol*. In a 250 mL, 3-neck flask fitted with an addition funnel, N_2 inlet, and magnetic stirring bar were placed 5.0 g (4 mmol) *m*-hydroxybenzyl alcohol and 4 mL (14.5 g, 143 mmol) Et_3N in 100 mL CH_2Cl_2. After cooling to 0°, 10 ml (14.8 g, 129 mmol) of freshly distilled methanesulfonyl chloride in 20 mL CH_2Cl_2 was added dropwise.[27] Then stirring was continued an additional 10 min. The soln was poured into a separatory funnel and was washed with ice water, 5% H_2SO_4, sat $NaHCO_3$ aq, and brine, in that order. The organic layer was then dried over $MgSO_4$, and the solvent was removed under reduced pressure to give 9.9 g (35 mmol) of bismethanesulfonate as a white crystalline solid in 87% yield.

^{1}H NMR (90 MHz): δ 5.76–7.2 (m, 4H), 5.37 (s, 2H), 3.12 (s, 3H), 2.95(s, 3H).

In a 250 mL, 3-neck, roundbottom flask fitted with a magnetic stirring bar, N_2 inlet and reflux condenser were placed 5.0 g (17.8 mmol) of the above sulfonate ester, 150 mL MeOH and 3 g (55 mmol) NaOMe. The soln was heated to reflux for 1 hr, then 25 mL of 33% NaOH aq was added and the mixture was heated at 80° for an additional 30 min. The soln was then cooled to room temp, poured into a separatory funnel, and extracted with Et_2O; the organic layer was discarded. The aqueous layer was then acidified with conc HCl and extracted with Et_2O. The ether layer was washed with brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. NMR analysis of the residue shows it to be **27**. The spectrum was identical with that of **27** obtained from **8b**.

MS parent *m/e* = 138; base peak 107 (–OCH_3). ^{1}H NMR (90 MHz): δ 5.73–7.0 (m, 1H), 6.95–6.55 (m, 3H), 4.39 (s, 2H, $C\underline{H}_2O$), 3.35 (s, 3H, $OC\underline{H}_3$). This material was purified by GC on SE-30 to provide an analytical sample. (Found: C 79.23, H 5.74. Calcd. for $C_8H_{10}O_2$: C 79.23, H 5.70%).

Alcoholysis of **14**

(a) *Thermal*. A sample of 30 mg of **14** was heated 150° in 10 mL ethylene glycol for 1 hr, after which the mixture was taken up in ether and washed with H_2O. The organic layer was dried over $MgSO_4$, and the solvent was removed *in vacuo* to yield **28** quantitatively (NMR).

^{1}H NMR ($CDCl_3$, 90 MHz): δ 6.8–8.2 (m, 6H), 6.54 (br, s, 1H), 4.66 (s, 2H), 3.76 (m, 2H), 3.67 (m, 2H), 2.64 (br, s, 1H); MS (*m/e*): 218 (42.1); 157 (100); M_r: 218.0938; Calcd. for $C_{13}H_{14}O_3$: 218.0943.

(b) *Photolytic*. A sample of 50 mg of **14** in 20 mL MeOH was photolyzed for 30 min at 350 nm in a Rayonet photochemical reactor at 0°. The solvent was removed *in vacuo* to yield (by NMR analysis) pure **29**, m.p. 125–126°.

^{1}H NMR ($CDCl_3$, 90 MHz): δ 6.8–8.2 (m, 6H), 5.66 (s, 1H), 4.58 (s, 2H), 3.42 (s, 3H); MS 188 (91.7), 157 (100); MS M_r 188.0856; Calcd. for $C_{12}H_{12}O_2$: 188.0837.

Synthesis and EPR spectrum of 6-methylenebicyclo[3.1.0]*hexan-2-one-3-ene*-^{17}O (**8b**–^{17}O). In a dry 5 mL RB flask ketal **13** (45 mg/0.3 mmol) was dissolved in 2 mL dry ether. To this soln, 40% enriched $H_2{}^{17}O$ (25 μL/1.4 mmol) was syringed in followed by 0.5 mL of a 0.5 N HCL:Et_2O soln. The turbid soln was stirred for 10 min and then solid K_2CO_3 was added. The product was then isolated by preparative GC (1.5% OV 101). GC/Mass spectral analysis of the ethereal soln showed ~30% ^{17}O incorporation. The GC isolated sample was then dissolved in 250 μL dry 2-methyl THF and pipeted into a quartz ESR tube. The sample was degassed by 3 freeze-pump-thaw cycles and sealed under vacuum. Irradiation (λ > 310 nm) of this soln at 30K in the cavity of an EPR spectrometer displayed the triplet spectrum of the *m*-methylenephenoxyl diyl with some added absorptions in ΔMs = ±1 region around 3030 and 3480 G. (9.086 GHz microwave frequency). This sample was repurified by VPC (1.5% OV 101) and dissolved in dry benzene. The same spectrum observed in this solvent upon photolysis in the EPR cavity at 30K.

3, 4-*Benzo-6-methylenebicyclo* [3.1.0] *hexan-2-one-3-ene*-^{17}O. (**14**–^{17}O). In a similar manner, 12 mg of **16** was placed into a dry 25 ml round bottom flask flushed with N_2. To this was added 3.5 ml $H_2{}^{17}O$ (40% ^{17}O enriched) and 1 ml a 0.25M soln of dry HCl in THF. This soln was stirred for 1 hr and subsequently diluted with dry THF and dried over K_2CO_3. With stirring, oven dried $NaHCO_3$ was slowly added to neutralize excess acid after which the solid was filtered off under N_2. The solvent was removed *in vacuo* to yield 8.9 mg (95%) of the labeled ketone **14**–^{17}O. Mass spectral analysis showed it was 32.1% enriched with ^{17}O.

Optical activation of **8b** (Scheme III). The chloroketal **11** (3.3 grams/17.5 mmol), dissolved in 30 mL THF, was treated with 5% H_2SO_4 (30 ml), and the heterogenous mixture was vigorously stirred for 2 hr at room temp. The mixture was then transferred to a separatory funnel with the aid of 50 ml ether. The layers were separated, and the organic layer was washed successively with 2 × 30 mL, $NaHCO_3$ aq, 1 × 30 mL H_2O and 1 × 30 mL brine. The organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo* to yield 2.4 g (95%) of 6-methyl-6-chlorobicyclo[3.1.0]hexan-2-one as a light yellow oil.

^{1}H NMR (90 MHz) $CDCl_3$: δ 2.15 (br, s, 3H), 2.1–1.5 (m, 3H), 1.58 (s, 3H); MS (*m/e*): 146 (M + 2), 144 (M), 118, 116, 104, 102 (base peak), 81.

The chloroketone (500 mg/3.5 mmol) and 0.3 mL (*D*(–) 2,3-butanediol, $[\alpha]_D$ + 12.5° (neat), were dissolved in 30 mL of benzene. A small crystal of toluenesulfonic acid was added, and the soln was refluxed for 10 hr with a Dean-Stark trap. The mixture was then transferred to a separatory funnel with the aid of 50 ml ether. The layers were separated and the organic phase was washed successively with 1 × 25 mL $NaHCO_3$ aq, 2 × 40 mL H_2O, and 1 × 30 mL brine. The organic phase was dried over $MgSO_4$ and the solvent removed *in vacuo* to give 575 mg (77%) of the corresponding ketal.

^{1}H NMR (90 MHz, $CDCl_3$): δ 3.5 (m, 2H), 2.1–1.4 (m, 6H), 1.55 (s, 3H), 1.22 (d, 6H); MS (*m/e*): 218 (m + 2), 216 (M), 190, 188, 181, 154, 114 (base peak), 109.

Fractionation of the four-component mixture of diastereomers was achieved by GC of the butanediol ketal mixture with a 10 ft x ¼-in 5% Carbowax M column (flow 60 mL/m, column temp 125°). The components of the major diastereomeric pair of ketals, derived from the 90% component of the ketone mixture, emerged with retention times of 48.5 m (fraction A) and 51 m (fraction B). Fraction A consisted of an approx. 2:1 mixture, the smaller component being the same isomer that appeared in fraction B

Table 4. Photolysis of optically active **8b**

Run	Glass	T, K	total, irrad. time, s	No. of cycles	$[\alpha]_{365}$, deg
0	——	——	0	0	−2340 ± 37
1	3 MP	20	120	2	−2290 ± 286
2	2MeTHF	25	290	3	−2270 ± 39
3	2MeTHF	30	1374	10	−2700 ± 380

(270 MHz NMR analysis). Fraction B contained little if any cross-contaminant from fraction A by this criterion. The components of the minor pair of diastereomers, from the 10% component of the ketone mixture, were not adequately separated by this column.

Fraction A, (120 mg/0.6 mmol) was dissolved in 5 mL dry ether and cooled to 0°. Br_2 (30 μL/0.6 mmol) was syringed into the stirred soln. The ice bath was removed and the reaction was stirred for 0.5 hr. The mixture was then transferred to a separatory funnel with the aid of 10 mL ether. The layers were separated and the organic layer was washed successively with 2 × 10 mL H_2O 2 × 10 mL $NaCO_3$, 1 × 10 mL H_2O and 1 × 10 mL brine. The organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The oily residue was immediately dissolved in 5 mL dry DMSO, and added to a 50 mL 3-neck flask containing BuOK (0.3 g/2.6 mmol) dissolved in 10 mL dry DMSO. The mixture immediately turned black and was then heated to 70° for 90 min with stirring under N_2. The reaction was quenched with 10 mL H_2O, and the aqueous layer was repeatedly extracted with pentane (8 × 10 mL). The combined pentane extracts were washed with 2 × 10 mL H_2O and 1 × 10 mL brine. The organic phase was dried over $MgSO_4$, filtered and evaporated to yield 85 mg (80%) of partially resolved ketal.

^{1}H NMR (270 MHz, $CDCl_3$): δ 5.95 (d × d, 1H), 5.22 (d, 1H), 5.13 (d, 2H), 3.56 (m, 2H), 2.4 (m, 1H), 2.06 (m, 1H), 1.25 (predominantly 2 sets of doublets, 6H); MS (*m/e*, on unresolved sample): 178 (M), 177, 124, 123, 106, 105, 90, 89, 78 (base peak).

The ketal (85 mg/0.48 mmol) was dissolved in 10 mL ether and vigorously stirred for 10 min with 5 mL a 5% HCl aq. The heterogenous mixture was then transferred to a separatory funnel with aid of 1 mL ether and the layers were separated. The organic phase was washed successively with 3 × 10 mL 5% $NaCO_3$ and 1 × 10 mL brine. The organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo* to yield 45 mg (88%) of **8b** as a light yellow oil. After preparative GC (OV-101 column), this material had a GC retention time and UV spectroscopic properties identical with those of racemic **8b**, $[\alpha]^{25}_{365} - 2340 \pm 37°$, $[\alpha]^{25}_{589} - 227 \pm 25°$ (cyclohexane); UV λ_{max} (nm, ϵ, cyclohexane) 376 (37), 359 (100), 344 (103), 329 (87), 245 (3260).

Low temperature photolysis of optically active ketone **8b**. A small sample of **8b** (1–2 mg) was purified by GC (OV 101) and dissolved in 250 μL of distilled 2-methyltetrahydrofuran (2-MeTHF) or 3-methylpentane (3 MP). This soln (0.037–0.075M) was pipeted into a quartz ESR tube, degassed by 3-freeze-pupm-thaw cycles and sealed *in vacuo*. The tube was placed in the cavity of a Varian E-9 EPR spectrometer and cooled to 30K. The sample was then photolyzed (Hanovia 200 W high pressure lamp, $CuSO_4$ filter) directly in the cavity. Coincident with photolysis. the characteristic triplet spectrum of *m*-methylenephenoxyl was observed and reached maximum intensity after 1.5 min irradiation. The sample was then removed from the cavity and allowed to warm to room temp. The samples were recooled and photolyzed in similar manner. A small decrease in the triplet signal intensity was observed upon rephotolysis.

When the above procedure was carried out with 3 MP as the glass, an extremely weak EPR triplet signal was observed with a large g = 2 doublet impurity. Upon warming a flocculent white polymeric material was observed.

After the photolytic cycles were complete, **8b** was repurified by GC (OV 101), and the samples were dissolved in a 1 mL (runs 1 and 2) or 2 ml (run 3) volumetric flask with spectral grade cyclohexane. The optical rotations were then measured at 5 wavelengths (Perkin–Elmer 241 digital read-out polarimeter). The concentrations were then determined by the appropriate dilution (spectral grade cyclohexane) such that the UV absorptions at λ_{max} 329 nm, ϵ = 87.1, and λ 252 nm, ϵ = 25900, could be measured. The data are displayed in Table 4.

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