Table II. Rates of $5 \rightarrow 9 + 10$

T, °C	271.5	274.25	281.25	285.0	286.4	292.5	297.5	303.0
$k \times 10^4$	0.904	1.13	1.85	2.59	2.85	4.45	6.62	9.89
$(10 + 11)/9$	1.50	1.52	1.545	1.575	1.59	1.63	1.70	1.77

Table III. Activation Parameters

	$\log A$	$E_a{}^a$	$\Delta H^{\ddagger\, a,b}$	$\Delta S^{\ddagger\, b}$	$\Delta G^{\ddagger\, a,b}$
$1 \rightarrow 2 + 3$	16.1 ± 0.1	58.0 ± 0.4	56.8	11.7	49.6
$4 \rightarrow 7$	14.75 ± 0.2	51.7 ± 0.6	50.5	5.6	47.2
$5 \rightarrow 9 + 10$	14.95 ± 0.2	47.4 ± 0.5	46.3	6.7	42.5
$5 \rightarrow 9$	13.75 ± 0.1	45.35 ± 0.3	44.2	1.2	43.6
$5 \rightarrow 10$	15.2 ± 0.2	48.55 ± 0.4	47.4	7.8	43.1

[a] kcal/mol. [b] Calculated for mean temperatures: 339.7 °C for 1, 322.0 °C for 4, and 286.3 °C for 5.

Table IV. Ratios $(10 + 11)/9$ (at 270 °C)

	gas added		
reaction time, min	none (4 mm neat)	argon (200 mm)	I (60 mm) + argon (140 mm)
20	0.80	0.96	1.49
60	0.54	0.81	1.48
160	0.42	0.60	1.50

significant fraction of the reaction proceeded via an extrusion of CF_2:.[12] The overall rates of rearrangement of **5** for eight temperatures[8] are given in Table II, along with the observed ratios of (a):(b) as measured by the ratios of $(\mathbf{10} + \mathbf{11})/\mathbf{9}$.

The rearrangement of **5** to **9** proceeds 140 times faster than that of difluorospiropentane (**1**) at 340 °C. This enhancement amounts to a $\Delta\Delta G^{\ddagger}$ of 6.0 kcal/mol, a value which is comparable to that of the tetrafluoromethylenecyclopropane system wherein the second CF_2 group gives rise to a $\Delta\Delta G^{\ddagger}$ of 7.4 kcal/mol for homolysis of the bond *between* the CF_2 groups.[2] Thus, it appears that while a single CF_2 group in a cyclopropane ring does not lead to a significant weakening of bonds adjacent to it, *two* such groups do indeed cause a substantial weakening of that adjacent bond between them.

The extrusion of CF_2: from **5** is probably a concerted process, although involvement of intermediate **8** cannot be rigorously excluded. Why should extrusion compete effectively with rearrangement in the case of **5** when it did not for either **1** or **4**? The answer comes from the fact that while adding the second CF_2 group enhances rearrangement by 6 kcal/mol, it is expected to enhance CF_2: extrusion by *~8 kcal/mol.* This expectation derives from the known relative propensities of 1,1-difluorocyclopropane ($\log A = 14.1$, $E_a = 56.4$ kcal/mol) and 1,1,2,2-tetrafluorocyclopropane ($\log A = 15.3$, $E_a = 48.5$ kcal/mol) to extrude CF_2:.[13b] In fact, at 340 °C, **5** loses CF_2: at about the same rate (a factor of 0.80) as does 1,1,2,2-tetrafluorocyclopropane.

An unexpected and mechanistically significant pressure dependence on the ratio of (a):(b) was detected in this reaction. As has been reported earlier, the extrusion of CF_2: from difluorocyclopropanes is a *reversible* process, and in order to determine accurate rates for processes a and b it was necessary to add a CF_2: trapping agent. Isobutylene (I) was chosen because of its known ability to irreversibly add CF_2: at these temperatures. The addition of I did indeed eliminate return of CF_2: and allowed good first-order kinetics to be observed for the thermal processes of **5**. However, very noticeable was a *sharp increase* in the ratio of (a):(b) (as measured by the ratio of $(\mathbf{10} + \mathbf{11})/\mathbf{9}$ not only when I was added but also, although less dramatic, when an inert gas was added (see Table IV)). While an increase in ratio was to be expected for the addition of I, due to the inhibition of return of **10** to **5**, the effect of added argon was unexpected. A number of control experiments served to elucidate the cause of these effects.

First, the rate of decomposition of **5** was found to be *independent* of trapping agent concentration. Second, 2,3-dimethyl-2-butene (T) had a relative trapping efficiency of 2.03 relative to I. These experiments rule out direct interaction of trapping agent with either **5** or intermediate **6**[15] and indicated that the alkene was merely trapping CF_2:.

If, in the absence of trapping agent, CF_2: returned to **5** via addition to **10**, why then is there no concomitant addition to **11** able to be observed? (**10** and **11** rapidly equilibrate under the reaction conditions.[18]) It was able to be demonstrated in a control study that CF_2: adds to **10** 40 times faster than to **11**. With the ratio of **10**:**11** = 4.3, the rate of addition to **11** should be only $^1/_{170}$ that of addition to **10**; hence, it is undetectable.[19]

The effect of added inert gas is most easily explained if one assumes that when CF_2: is extruded from **5**, it is formed *in a vibrationally excited state.* Under low-pressure conditions the "hot" CF_2: is consumed, relatively indiscriminately, either by addition to **10** (return to **5**) or by dimerization (formation of TFE). However, when "cooled" by collision with any diluent gas, the CF_2: becomes more discriminating in its reactions and shows a greater preference for the dimerization process which has almost no E_a associated with it.[20] This hypothesis is strongly supported by our observation that under *neat* conditions (4 mm of **5**) the ratio of **9**/TFE = 10.9, after ~160 min at 270 °C, and the $(\mathbf{10} + \mathbf{11})/\mathbf{9}$ ratio is 0.42, while in the presence of 200-mm argon under the same conditions, **9**/TFE = 6.8 and $(\mathbf{10} + \mathbf{11})/\mathbf{9} = 0.60$.

Hexafluorospiropentane and perfluorospiropentane have been synthesized and are currently under kinetic investigation. Upon completion of this work a full report and discussion on the incremental effects of CF_2 groups on spiropentane thermolyses will be forthcoming.

Acknowledgment. We thank the National Science Foundation for partial support of this research.

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(10) Spectral properties of **9**: NMR ($CDCl_3$) δ 2.3-3.1 (complex m); ϕ 91.11 (complex m), 85.0 (midpoint) (AB with further splitting, $J_{AB} = 36$ Hz, $\Delta\nu_{AB} = 780.8$ cm^{-1}). Mass spectroscopy gave M$^+$ as 140.02404 [standard deviation = 0.00191 (13.6 ppm)]. Calculated M$^+$ was 140.02491 [deviation = 0.00087 (6.2 ppm)].

(11) Products **7** and **9** were found *not* to be thermally interconvertible under the reaction conditions.

(12) The extrusion of CF_2: from fluorine-substituted cyclopropanes is a well-known process.[13]

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(14) The errors given are standard deviations and demonstrate the good precision of the data. The accuracy of the activation parameters is, however, somewhat less certain; we would estimate $\log A \pm 1$ unit, and $E_a \pm 1$ kcal/mol.

(15) Diradical **6** should be intercepted more rapidly by I than by T,[16] while CF_2: has been shown to be trapped more efficiently by T.[17]

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(19) This control was run at 180 °C (the temperature at which HFPO decomposes). Hence the ratio of reactivity at ~270 °C where most of our control reactions with **5** were run should be somewhat smaller.

(20) Dalby, F. W. *J. Chem. Phys.* **1964**, *41*, 2297.

The Cation-Radical Catalyzed Diels-Alder Reaction

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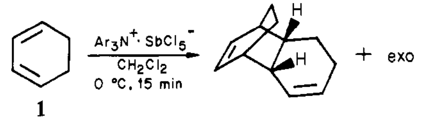
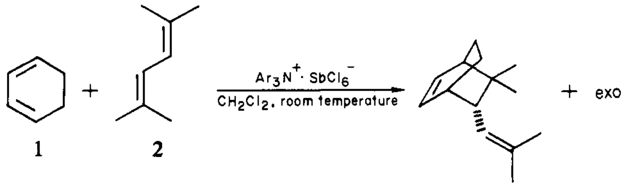
The especially high reactivity of electron-deficient dienophiles in the Diels-Alder reaction is a familiar characteristic of this strategic synthetic reaction.[1] Although Lewis acids can enhance the reactivity of some dienophiles containing oxygen-bearing functionality,[2] the inherent inefficiency of reactions involving approximately neutral or electron-rich dienophiles imposes a major constraint on the generality of the Diels–Alder reaction. The premise upon which the present work was based is that this reactivity constraint might be relieved by conversion of these dienophiles to their corresponding cation radicals which, being rather highly electron-deficient species, might add readily to appropriate cisoid dienes. The neutral and electron rich subsets of dienophiles are just those which are most readily ionized to cation radicals. This qualitative premise has proved heuristic and apparently even literally valid in the case of dienophiles which are conjugated dienes.

The Diels–Alder dimerization of 1,3-cyclohexadiene (**1**) has been effected in 30% yield after 20 h at 200 °C.[3] When **1** is exposed to catalytic (5–10 mol %) quantities of the stable cation-radical salt tris(*p*-bromophenyl)aminium hexachlorostibnate[4] in methylene chloride at 0 °C, Diels–Alder-type dimerization occurs in 70% yield within 15 min.[5] The endo/exo selectivity ratio (5:1) is similar to but slightly greater than that observed (4:1) in the uncatalyzed Diels–Alder reaction. The reaction can be carried out at temperatures ranging from −78 °C to ambient without appreciable loss of efficiency. In this and all subsequent reactions reported herein the products were isolated by GC collection and characterized by MS, GC MS, ^1H and ^{13}C NMR, and, wherever feasible, by comparison with samples prepared via the uncatalyzed Diels–Alder reaction.



(5:1)

A second limitation of the uncatalyzed Diels–Alder reaction is its pronounced sensitivity to steric effects.[1] As an illustration of the kinetic impetus of the cation-radical Diels–Alder reaction and the expanded steric scope of this reaction, the subjection of equimolar quantities of **1** and the sterically hindered dienophile 2,5-dimethyl-2,4-hexadiene (**2**) to cation-radical conditions affords a 40% yield of the endo/exo adduct pair **3**. Note that the quaternary carbon at C_5 is installed with relative ease.

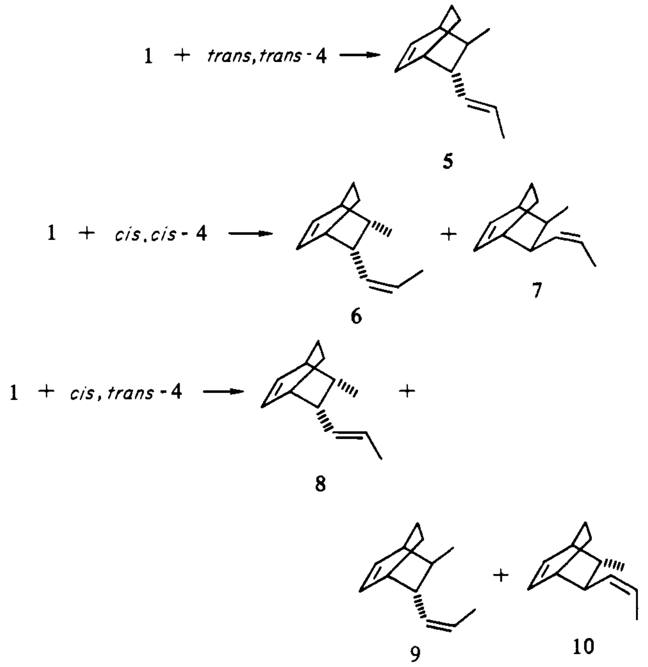


3

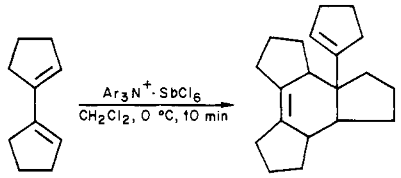
(4:3)

The previous two examples demonstrate that the endo selectivity principle characteristic of the Diels–Alder reaction is qualitatively retained in the cation-radical catalyzed process. An even more critical question is whether the new reaction retains the reliable suprafacial stereospecificity associated with the uncatalyzed reaction. The reactions of **1** with each of the three geometric isomers of 2,4-hexadiene (**4**) were therefore studied (Scheme I). As previously, a 1:1 mixture of **1** and **4** was subjected to cation-radical catalysis conditions. Reaction was complete within 1 h. At intermediate times, recovery and analysis of unreacted diene revealed no more than traces of equilibration with the other diene geometric isomers. Reaction with *trans,trans*-**4** yields a single stereoisomer, the endo, trans adduct **5**, in 20% unoptimized yield, in addition to 40% of the dimer of **1**. Similarly, *cis,cis*-**4** yields only the cis, endo/exo adduct pair **6** and **7**, and *cis,trans*-**4** yields **8**, **9**, and **10**. Significantly, the exo isomers are observed only where the propenyl moiety is cis. A steric effect destabilizing the otherwise highly favored endo transition state appears likely in these specific instances. The uncatalyzed Diels–Alder reaction yielded both members of the endo/exo pair in each case in yields of 0.5–2% after 2 days at 200 °C. The suprafacial stereospecificity of the cation-radical Diels–Alder reaction is evident and no less impressive than that of the uncatalyzed reaction.

Scheme I



The cation-radical Diels–Alder reaction is also successful with dienes (in the dienic role) which are not rigidly cis, as illustrated by the facile dimerizations of 1,1′-dicyclopentenyl (**11**) and 1,1′-dicyclohexenyl. The Diels–Alder dimer of **11**, for example, is obtained in 50% yield (GC analysis, also GC collected in 35% yield).



11 (exo + endo)

The reaction between **1** and **2** described above is believed to be mechanistically significant. The dimer of **1** is formed in only rather modest amounts (20% yield) in this reaction, in contrast to the reaction of **1** and **4**, in which the dimer of **1** is the major product (40% yield). This observation is consistent with the formation of relatively minor amounts of the cation radical of **1** in the former reaction. This would, of course, be expected on the basis of the greater degree of alkyl substitution on the diene moeity of **2** than **1**. The adduct **3** then most logically arises, at least primarily, from reaction of the cation radical of **2** with neutral **1**. The tentative conclusion is therefore that the pericyclic step of the cation-radical Diels–Alder reaction involves (at least in this instance) the cation radical of the dienophile and the neutral diene, rather than conversely. The latter would be a [3 + 2] cycloaddition, whereas the former could be classified as either [4 + 1] or $[4 + 2]^{+\cdot}$, depending upon whether the positive charge resides mainly in the pericyclic system (**12**) or on the extrapericyclic

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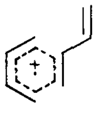
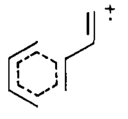
(5) The diene concentration does not appear critical. Concentrations in the range 0.1–0.4 M have been used successfully. Less than 5% catalyst normally results in incomplete or very slow reaction, but catalyst concentration does not appear to have a major effect on the yield or nature of the product.



12

[4 + 1]



13

$[4 + 2]^{+\cdot}$

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

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

$$\left.\begin{array}{l}\mathrm{DP^{+\cdot}} + \mathrm{D} \rightarrow \mathrm{A^{+\cdot}} \\ \mathrm{A^{+\cdot}} + \mathrm{DP} \rightarrow \mathrm{A} + \mathrm{DP^{+\cdot}}\end{array}\right\}\text{propagation}$$

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.

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

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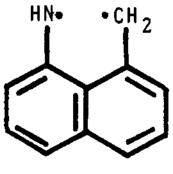
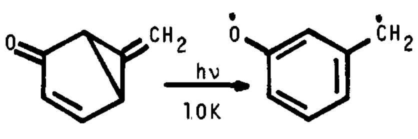
A challenging experimental and theoretical problem in the study of biradicals[1] (or, more generally, of multiradicals) is the identification of the total electronic spin of the ground state. For those conjugated π systems in which a degeneracy or near degeneracy of singly occupied orbitals occurs,[2] 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 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, $|D|/hc = 0.0266\ \mathrm{cm^{-1}}$, 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.



1



2 3

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 $\mathrm{cm^{-1}}$) $|D|/hc = 0.0204 \pm 0.0002$ 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 $0.022\ \mathrm{cm^{-1}}$, 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-^{17}O, generated by irradiation of 6-^{17}O, ~40% enriched,[17a] which in turn is prepared

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(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.

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