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Activation Energy of a Biradical Rearrangement Measured by Photo-CIDNP

Martin Goez* and Isabell Frisch

Fachbereich Chemie, Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes-Strasse 2,
D-06120 Halle/Saale, Germany

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Chemically induced dynamic nuclear spin polarizations (CIDNP) in the Paterno−Büchi cycloadducts of benzoquinone with norbornadiene or quadricyclane stem from a triplet biradical ^{3}III with a norbornenyl substructure. Intersystem crossing of ^{3}III and combination of the radical termini afford an oxolane I. By a cyclopropylmethyl−homoallyl rearrangement, ^{3}III is converted into a Paterno−Büchi biradical ^{3}IV, which after intersystem crossing yields an oxetane II. The ratio of nuclear spin polarizations in I and II strongly depends on temperature through the competition of nuclear spin relaxation in ^{3}III with the biradical rearrangement. Using a kinetic treatment, a closed-form expression for the polarization ratio was derived. The activation energy of the cyclopropylmethyl−homoallyl rearrangement (17 ± 2 kJ/mol) was obtained from an evaluation of the CIDNP signals.

Introduction

Nuclear spins are nearly ideal labels for mechanistic and kinetic investigations of chemical reactions. Owing to their tiny magnetic energies, they disturb neither equilibria nor rates, and a highly specific mode of detection, nuclear magnetic resonance, is available for them. CIDNP (chemically induced dynamic nuclear polarizations)[1] spectroscopy is a typical example. Polarizations (i.e., nonequililibrium populations of the nuclear spin states) are produced in radical pairs or biradicals by the interplay of nuclear-spin selective intersystem crossing and electron-spin selective chemical reactivity and are then observed in subsequent diamagnetic species by NMR.

Although the polarizations persist in the diamagnetic reaction products for the spin−lattice relaxation time (seconds for protons), CIDNP generation is completed within the lifetime of the paramagnetic intermediates (nanoseconds); hence, the method is sensitive to faster processes than is time-resolved EPR. Its application to laser-flash photolysis ("flash CIDNP")[2] is especially attractive because it combines ultrafast photochemical generation of the active species with the analytical potential of Fourier transform NMR. The duration of the probing NMR pulse limits the time resolution of flash CIDNP to about 100 ns. However, much faster rates can be determined by using a competing chemical or physical process as an internal clock.[3] The present work is an example of the latter; the rate of rearrangement of a triplet biradical to a configuration that rapidly undergoes intersystem crossing and thus acts as a chemical sink is gauged against that of nuclear spin relaxation, which is related to the rotational correlation time of the molecule.

The biradical studied is a key intermediate in the Paterno−Büchi reaction of carbonyl compounds with quadricyclane Q or norbornadiene N.[4−7] A detailed understanding of this cycloaddition is important because it is a major parasitic reaction in the sensitized interconversion of Q and N, which is of potential interest in solar energy storage.[8] We have recently presented a detailed mechanistic investigation of the photoreaction of quinones with Q and N by CIDNP spectroscopy in which we employed the nuclear spins as labels to trace the pathways of formation, rearrangement, and decay of the intermediate biradicals.[7] In the present work, we use the polarization intensities and their temperature dependences to measure the activation barrier of the biradical rearrangement.

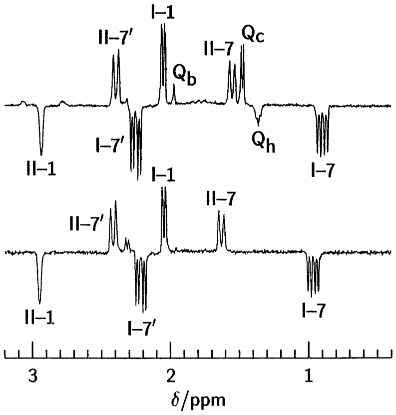

Figure 1. CIDNP during photoreactions of benzoquinone with quadricyclane in acetonitrile (top trace) and chloroform (bottom trace). The assignment of the protons in the products I and II refers to the structural formulas given in Scheme 1. The signals Q_c, Q_b, and Q_h belong to the protons on the cyclobutane ring, the bridge, and the bridgehead carbons. With the chosen numbering, this would correspond to protons $H^{2,3,5,6}$, $H^{7,7'}$, and $H^{1,4}$ in the cycloadducts.

Results and Discussion

CIDNP Spectra and Reaction Mechanism. Figure 1 displays two examples of ^{1}H CIDNP spectra observed on laser excitation of benzoquinone B with quadricyclane Q as the quencher; one spectrum was obtained in a polar solvent, and the other, in a nonpolar solvent. Only the region of the most strongly polarized signals is shown. With norbornadiene N instead of Q, the same CIDNP spectrum as with Q in the second case is recorded, regardless of which solvent is actually used. Generally, the signal-to-noise ratio is found to be lower in a less polar solvent and is also significantly lower for N than for Q.

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* Corresponding author. E-mail: goez@chemie.uni-halle.de.

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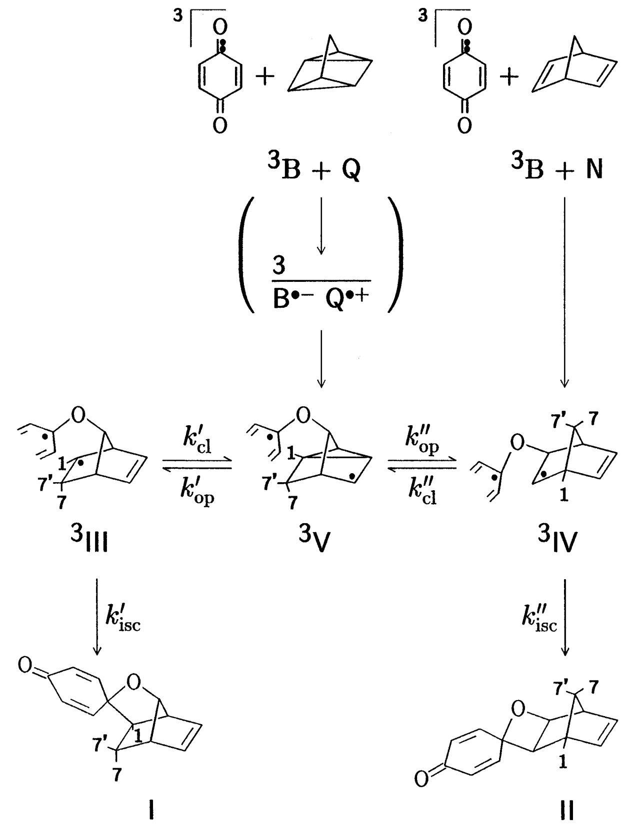
SCHEME 1



The reaction mechanism concluded from our CIDNP experiments[7] and the structural formulas of the reactants, intermediates, and products are given in Scheme 1. Corresponding protons in species I−^{3}V bear the same number; for this, a nonstandard method of numbering had to be chosen.

CIDNP predominantly arises from biradical ^{3}III in this system. Despite their source, the polarizations are of the radical pair (i.e., ST_0) type, which is an exceptionally rare phenomenon for such a short-chain biradical. After intersystem crossing of ^{3}III, combination of the radical termini produces oxolane I. A 1,2 shift of a vinyl group (i.e., a cyclopropyl−homoallyl rearrangement) reversibly converts ^{3}III into another biradical, ^{3}IV. The latter has a significantly higher rate of intersystem crossing, and its ring closure to give oxetane II thus provides the analogue to the escape reaction of freely diffusing radical pairs in CIDNP. The interconversion of ^{3}III and ^{3}IV involves yet another biradical, ^{3}V, as an intermediate.

The substrate determines which biradical is formed initially. With N, the paramagnetic stage is entered at ^{3}IV, which results from quenching of the quinone triplet by the hydrocarbon; with Q, this reaction instead leads to ^{3}V. As an additional mechanistic complication that occurs with Q only, in a polar solvent, electron transfer precedes biradical formation. Under these circumstances, ^{3}V is produced by a geminate reaction of the spin-correlated radical pair $\overline{B^{\bullet-}Q^{\bullet+}}$ consisting of the radical anion of the quinone and the radical cation of the hydrocarbon. In its triplet state, this pair combines to give the triplet biradical because no other chemical deactivation channels are open to it, whereas in its singlet state, it undergoes electron return instead, which allows it to regain the quinone B and the substrate Q, both in spin-polarized form. Although these polarizations are seen to be quite pronounced in the displayed spectrum, their transfer to cycloadducts I and II is negligible for benzoquinone, as opposed to that for other sensitizers.

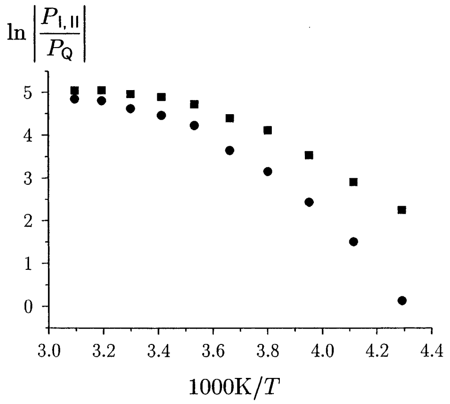


Figure 2. Photoreaction of benzoquinone and quadricyclane in acetonitrile. Arrhenius plots of the polarization intensities P of H^7 in I (■) and II (●) relative to the polarization intensity of the cyclobutane protons in the regenerated quencher Q.

Experimental Temperature Dependence. The temperature at which the spectra are obtained has a marked influence on their appearance. The product polarizations significantly increase with temperature, by a factor of more than 50 over the range of our measurements (233−323 K). However, this increase is different for the two photoadducts, with II exhibiting a stronger temperature dependence than I. In contrast, the polarizations of Q that are regained from the radical ion pairs depend only weakly on temperature; at 323 K, they are about half as intense as at 233 K.

It is known that CIDNP enhancement factors are functions of temperature through their dependence on the diffusion coefficients D,[1] with absolute polarizations being approximately proportional to $D^{-1/2}$.[9] At the limiting temperature of our experiments, a ratio of less than 4 is estimated for D with the Stokes−Einstein equation and the known[10] viscosities of acetonitrile. After correcting for this effect, the polarization of Q remains practically constant throughout the temperature range considered.

The evaluation of absolute CIDNP signal strengths, especially for different samples, is not very accurate; small variations of the sensitizer concentration, fluctuations of the light intensity, or slight changes with temperature in the extinction coefficients at the excitation wavelength can easily cause unacceptably large errors. For these reasons, it is much more advantageous to compare relative CIDNP intensities, thereby eliminating this influence. One way to do this is to evaluate the ratios of the polarizations in the two products; another is to use the nearly constant peak Q_c as a convenient reference. Arrhenius plots of the signals I-7 and II-7 relative to Q_c are given in Figure 2. The significant curvature of these graphs cannot be explained by a different temperature dependence of CIDNP enhancement factors for the radical ion pair $\overline{B^{\bullet-}Q^{\bullet+}}$ and biradical ^{3}III, which are responsible for CIDNP of the starting materials and the products, respectively. Rather, we must attribute them to the complex reaction mechanism.

In the solvent $CDCl_3$, the same temperature dependence of the product polarizations is observed as in acetonitrile. However, as ^{3}III is formed without the intervention of radical ions in this system, no CIDNP signals of Q appear in $CDCl_3$, so the correction for the number of quanta absorbed cannot be performed, and there is a somewhat larger scatter of the data. Therefore, these results have not been included in Figure 2. The alternative approach, using the ratios of the polarizations in I and II, will be pursued below.

Kinetic Treatment. Regardless of the pathway of biradical formation, the different temperature dependence that is observed for the CIDNP intensities of I and II in the reaction with B (see Figure 2) cannot originate in a stage of the reaction preceding the biradical because this intermediate is the predominant source of these polarizations. However, the spin-sorting mechanism of S−T_0-type CIDNP would make the singlet and the triplet biradicals bear opposite polarizations of exactly equal magnitude. Because we do not have more than one product from each exit channel, different CIDNP intensities of a particular proton in I and its counterpart in II can thus be ascribed only to nuclear spin relaxation in the paramagnetic intermediates.

The chemical transformations in this system are described by the system of differential equations following from Scheme 1. Product formation from singlet biradicals is instantaneous on the CIDNP time scale; hence, we identify a rate of product formation with that of intersystem crossing of the respective biradical, disregard singlet biradicals completely, and treat the intersystem crossing of ^{3}III and ^{3}IV as irreversible. Owing to this irreversibility, the differential equations for ^{3}III−^{3}V are decoupled from those for I and II. For geometric reasons, the formation of III and the formation of IV are the only monomolecular decay pathways open to V. Because intersystem crossing of ^{3}V thus has the same effect as an increased intersystem crossing rate of ^{3}III and ^{3}IV, it is assumed to be contained in these processes and has not been included separately in the kinetic scheme.

CIDNP arises from intersystem crossing rates that depend on the nuclear spin state, so the differential equations have to be set up for each nuclear spin configuration of species I−^{3}V. For those protons that are polarized strongly enough to permit quantitative evaluation (H^1, H^7, and $H^{7'}$), there are no complications from magnetic equivalence, neither in the intermediates nor in the products. Hence, for each of these protons, the polarization can be calculated by solving a system of six and, subsequently, another system of four differential equations for $^3\mathrm{III}_\alpha ... {}^3\mathrm{V}_\beta$ and $\mathrm{I}_\alpha ... \mathrm{II}_\beta$, respectively, where the index denotes the spin state of the proton in question and all spin-dependent quantities are averaged over the spin states of all other protons in the usual way.[1]

In its ^{3}III configuration, the triplet biradical undergoes intersystem crossing with a rate constant that we express as $k'_{\mathrm{isc}} \pm x$ to indicate that it is composed of a nuclear spin-independent and a nuclear spin-dependent contribution. The former k'_{isc} takes into account spin−orbit coupling as well as those differences in the Larmor frequencies of the two radical moieties that are due to the Δg term and the averaged hyperfine effects of all nuclei except the one observed. The nuclear spin-dependent contribution x, which may be a positive or negative quantity depending on the sign of the hyperfine coupling constant of the proton in question, is added to k'_{isc} if the proton has α spin and subtracted if it has β spin. k'_{isc} and x also comprise the effects of time-dependent separations and encounters of the radical termini. Intersystem crossing of ^{3}IV and ^{3}V is taken to be spin-independent because the polarization pattern in the products does not give any indication at all of a participation of these intermediates in CIDNP generation.[7] The reasons for this are negligible hyperfine coupling constants of the observed protons in these biradical configurations as well as a shorter life, which is most likely due to increased spin−orbit coupling in the Paterno−Büchi-type biradical ^{3}IV and to the higher energy content of the strained configuration ^{3}V. The rate constant of intersystem crossing of ^{3}IV is denoted as k''_{isc}; as explained above, intersystem crossing of ^{3}V is contained in k'_{isc} and k''_{isc}.

Because polarizations are concentration differences of identical chemical species with different nuclear spin states, a change of variables to sums and differences,

$$\Sigma_{\mathrm{M}} = [\mathrm{M}]_\alpha + [\mathrm{M}]_\beta \qquad (1)$$

$$\Delta_{\mathrm{M}} = [\mathrm{M}]_\alpha - [\mathrm{M}]_\beta \qquad (2)$$

with M = I...V is advantageous (for ^{3}III−^{3}V, we omit the triplet sign in this notation for clarity). Nuclear spin-dependent rate constants such as x transform sums into differences and vice versa, whereas nuclear spin-independent rate constants (all other rate constants in Scheme 1) never connect sum terms with difference terms and vice versa.

Nuclear spin relaxation is introduced after this change of variables; this process, which cannot be displayed in Scheme 1, destroys difference terms and leaves unchanged sum terms. Relaxation will be more important the longer the life of a biradical configuration and the larger the interactions between the nuclei and the unpaired electron. These are the same factors that favor the generation of nuclear spin polarizations. By reversing this argument, the absence of CIDNP from ^{3}IV and ^{3}V indicates relaxation in ^{3}IV and ^{3}V to be much less important than relaxation in ^{3}III. Hence, we consider relaxation in ^{3}III only (rate constant k'_{rel}).

Finally, driving terms have to be added to the first system of differential equations. For the substrates N and Q, the entry points to the biradical stage are ^{3}IV and ^{3}V, respectively. Because presaturation was applied[11] and the generation of polarizations in intermediates that are earlier than the biradicals can be neglected, the driving terms do not induce nuclear spin-dependent concentration differences but influence Σ_{IV} and Σ_{V} only. For complete generality, the two driving terms leading to ^{3}IV and ^{3}V are taken to be arbitrary functions Φ_{IV} and Φ_{V}.

The system of six differential equations for the linear combinations of the paramagnetic species is then Laplace transformed to give

$$\begin{pmatrix} -(s+a) & -x & 0 & 0 & c & 0 \\ -x & -(s+b) & 0 & 0 & 0 & c \\ 0 & 0 & -(s+d) & 0 & e & 0 \\ 0 & 0 & 0 & -(s+d) & 0 & e \\ g & 0 & h & 0 & -(s+f) & 0 \\ 0 & g & 0 & h & 0 & -(s+f) \end{pmatrix} \begin{pmatrix} \mathscr{L}(\Sigma_{\mathrm{III}}; s) \\ \mathscr{L}(\Delta_{\mathrm{III}}; s) \\ \mathscr{L}(\Sigma_{\mathrm{IV}}; s) \\ \mathscr{L}(\Delta_{\mathrm{IV}}; s) \\ \mathscr{L}(\Sigma_{\mathrm{V}}; s) \\ \mathscr{L}(\Delta_{\mathrm{V}}; s) \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \mathscr{L}(\Phi_{\mathrm{IV}}; s) \\ 0 \\ \mathscr{L}(\Phi_{\mathrm{V}}; s) \\ 0 \end{pmatrix} \qquad (3)$$

where the Laplace transform of a function $y(t)$ is abbreviated $\mathscr{L}(y(t); s)$, with the Laplace variable s and

$$\begin{array}{lll} a = k''_{\mathrm{isc}} + k'_{\mathrm{cl}} & b = k''_{\mathrm{isc}} + k'_{\mathrm{cl}} + k'_{\mathrm{rel}} & c = k'_{\mathrm{op}} \\ d = k''_{\mathrm{isc}} + k''_{\mathrm{cl}} & e = k''_{\mathrm{op}} & f = k'_{\mathrm{op}} + k''_{\mathrm{op}} \\ g = k'_{\mathrm{cl}} & h = k''_{\mathrm{cl}} & \end{array} \qquad (4)$$

Equation 3 can be readily solved using determinants. All of the resulting expressions have the same denominator $N(s)$, which cancels when ratios are formed.

Laplace transformation of the differential equations for the products leads to

$$\mathscr{L}\left(\frac{\mathrm{d}}{\mathrm{d}t}\Sigma_{\mathrm{I}};\, s\right) = k'_{\mathrm{isc}}\mathscr{L}(\Sigma_{\mathrm{III}};\, s) + x\mathscr{L}(\Delta_{\mathrm{III}};\, s) \tag{5}$$

$$\mathscr{L}\left(\frac{\mathrm{d}}{\mathrm{d}t}\Sigma_{\mathrm{II}};\, s\right) = k''_{\mathrm{isc}}\mathscr{L}(\Sigma_{\mathrm{IV}};\, s) \tag{6}$$

$$\mathscr{L}\left(\frac{\mathrm{d}}{\mathrm{d}t}\Delta_{\mathrm{I}};\, s\right) = x\mathscr{L}(\Sigma_{\mathrm{III}};\, s) + k'_{\mathrm{isc}}\mathscr{L}(\Delta_{\mathrm{III}};\, s) \tag{7}$$

$$\mathscr{L}\left(\frac{\mathrm{d}}{\mathrm{d}t}\Delta_{\mathrm{II}};\, s\right) = k''_{\mathrm{isc}}\mathscr{L}(\Delta_{\mathrm{IV}};\, s) \tag{8}$$

The long-time values of the concentrations of I and II are obtained by setting the Laplace variable s in eqs 5 and 6 equal to 0; the same procedure for eqs 7 and 8 yields the nuclear spin polarizations in the products.

Three of the respective transforms entering the right-hand sides of eqs 5−8, namely, those that are needed for the nuclear spin polarizations, have the same dependence on the driving terms:

$$\mathscr{L}(\Sigma_{\mathrm{III}};\, 0) = -\frac{k''_{\mathrm{cl}}\Phi_{\mathrm{IV}} + (k''_{\mathrm{cl}} + k''_{\mathrm{isc}})\Phi_{\mathrm{V}}}{N(0)}\, k'_{\mathrm{op}}\{k''_{\mathrm{cl}}k'_{\mathrm{op}}(k'_{\mathrm{isc}} + k'_{\mathrm{rel}}) + k''_{\mathrm{isc}}[k'_{\mathrm{cl}}k''_{\mathrm{op}} + (k'_{\mathrm{op}} + k''_{\mathrm{op}})(k'_{\mathrm{isc}} + k'_{\mathrm{rel}})]\} \tag{9}$$

$$\mathscr{L}(\Delta_{\mathrm{III}};\, 0) = \frac{k''_{\mathrm{cl}}\Phi_{\mathrm{IV}} + (k''_{\mathrm{cl}} + k''_{\mathrm{isc}})\Phi_{\mathrm{V}}}{N(0)}\, xk'_{\mathrm{op}} \times [k''_{\mathrm{cl}}k'_{\mathrm{op}} + (k'_{\mathrm{op}} + k''_{\mathrm{op}})(k'_{\mathrm{isc}} + k'_{\mathrm{rel}})] \tag{10}$$

$$\mathscr{L}(\Delta_{\mathrm{IV}};\, 0) = \frac{k''_{\mathrm{cl}}\Phi_{\mathrm{IV}} + (k''_{\mathrm{cl}} + k''_{\mathrm{isc}})\Phi_{\mathrm{V}}}{N(0)}\, xk'_{\mathrm{cl}}\, k'_{\mathrm{op}}\, k''_{\mathrm{op}} \tag{11}$$

From eqs 7−11, the polarization ratio $P_{\mathrm{I}}/P_{\mathrm{II}}$ is thus calculated to be

$$\frac{P_{\mathrm{I}}}{P_{\mathrm{II}}} = -1 - \frac{k'_{\mathrm{rel}}}{k'_{\mathrm{cl}}}\left[1 + \frac{k'_{\mathrm{op}}}{k''_{\mathrm{op}}}\left(1 + \frac{k'_{\mathrm{cl}}}{k''_{\mathrm{isc}}}\right)\right] \tag{12}$$

Equation 12 exhibits all the features expected for the spin-sorting mechanism of S−T$_0$-type CIDNP. The ratio of polarizations depends neither on the magnetic parameters (which enter x) nor on the driving terms (i.e., it is independent of whether N or Q were the starting materials); the result is negative, and for vanishing nuclear spin relaxation it approaches −1, as it must because I and II stem from different exit channels and are the only products.

The fourth Laplace transform $\mathscr{L}(\Sigma_{\mathrm{IV}};\, 0)$, which is needed for the product yield of II, can be calculated as above but does not have the same dependence on the input channel as do eqs 9−11. Hence, the product ratio depends on the entry point to the mechanism. Because with substrate Q isomerization to N might partly precede biradical formation, evaluation of the product distribution is, therefore, intrinsically less reliable than is evaluation of the polarization ratio.

Both eqs 5 and 6 contain terms ($k'^{2}_{\mathrm{isc}} - x^2$). Because the nuclear spin-dependent contribution to intersystem crossing is much smaller than the nuclear spin-independent contribution, x^2 can be neglected in these combinations. By setting either Φ_{IV} or Φ_{V} equal to 0, one obtains the theoretical product ratios with Q and N, ([II]/[I])$_{\mathrm{Q}}$ and ([II]/[I])$_{\mathrm{N}}$:

$$\left(\frac{[\mathrm{II}]}{[\mathrm{I}]}\right)_{\mathrm{Q}} = \frac{k''_{\mathrm{isc}}(k'_{\mathrm{cl}} + k'_{\mathrm{isc}})k''_{\mathrm{op}}}{k'_{\mathrm{isc}}(k''_{\mathrm{cl}} + k''_{\mathrm{isc}})k'_{\mathrm{op}}} \tag{13}$$

$$\left(\frac{[\mathrm{II}]}{[\mathrm{I}]}\right)_{\mathrm{N}} = \frac{k''_{\mathrm{isc}}}{k''_{\mathrm{cl}}}\left[1 + \frac{k''_{\mathrm{op}}}{k'_{\mathrm{op}}}\left(1 + \frac{k'_{\mathrm{cl}}}{k'_{\mathrm{isc}}}\right)\right] \tag{14}$$

Evaluation of the Temperature Dependence. Equation 20 can be further simplified. Because biradicals ^{3}III and ^{3}IV possess virtually the same heat of formation[7] and their structural differences are also minute, it is reasonable to assume that their rates of ring closure to give the cyclopropylmethyl moiety in ^{3}V are identical; the same should hold for the rates of the two reverse processes. Replacing, on these grounds, k'_{op} and k''_{op} by k_{open} as well as k'_{cl} and k''_{cl} by k_{close} yields

$$\frac{P_{\mathrm{I}}}{P_{\mathrm{II}}} = -1 - \frac{k'_{\mathrm{rel}}}{k_{\mathrm{close}}}\left(2 + \frac{k_{\mathrm{close}}}{k''_{\mathrm{isc}}}\right) = -1 - \frac{k'_{\mathrm{rel}}}{k_{\mathrm{close}}}\zeta(T) \tag{15}$$

As will be shown below, the term $\zeta(T)$ is only a weak function of temperature under our experimental conditions, so $P_{\mathrm{I}}/P_{\mathrm{II}}$ chiefly depends on the ratio of the rate constants for ring closure and nuclear spin relaxation of ^{3}III.

Because the skeleton rearrangement must be an activated process, we write k_{close} as $A\exp(-E_{\mathrm{a}}/RT)$. Under our experimental conditions,[12] k'_{rel} is directly proportional to the rotational correlation time τ_{r} of the biradical, τ_{r} in turn being proportional to η/T:

$$k'_{\mathrm{rel}} = \frac{3}{10}\left(\frac{\mu_0}{4\pi}\right)^2 \hbar^2 \gamma_{\mathrm{e}}^2\, \gamma_{\mathrm{n}}^2\, d_{\mathrm{eff}}^{-6}\, \frac{4\pi r^3}{3k_{\mathrm{B}}}\, \frac{\eta}{T} = mn\frac{\eta}{T} \tag{16}$$

(γ_{e} and γ_{n}, gyromagnetic ratios of the electron and proton, respectively; d_{eff}, the effective mean distance between them; r, molecular radius; η, solvent viscosity). Strictly speaking, eq 16 is valid for a radical only, not for dipolar relaxation of a proton by *two* interacting electrons in a biradical. However, the occurrence of strong S−T$_0$-type CIDNP shows that most of the time the interaction between the electron spins is negligible, in a way similar to that for a freely diffusing radical pair. A description in terms of independent radical moieties, which also formed the basis of the interpretation of the polarization patterns,[7] thus seems appropriate in this case.

By expressing η as $C\exp(E_{\mathrm{vis}}/RT)$, one obtains

$$\ln\left[\left(-\frac{P_{\mathrm{I}}}{P_{\mathrm{II}}} - 1\right)\frac{T}{\mathrm{K}}\right] = \ln\frac{mnC}{A} + \ln\zeta(T) + \frac{E_{\mathrm{a}} + E_{\mathrm{vis}}}{RT} \tag{17}$$

ln $\zeta(T)$ is a convex function of $1/T$. If the variation of this term with temperature can be disregarded, a plot of ln[$(-P_{\mathrm{I}}/P_{\mathrm{II}} - 1)T/\mathrm{K}$] against $1/T$ should be linear, with a slope of $(E_{\mathrm{vis}} + E_{\mathrm{a}})/R$; otherwise, the plot will show an upward curvature. As is seen in Figure 3, the polarization ratios exhibit the expected behavior. Because of the local C_s symmetry of the molecular fragment comprising the radical center and the CH^{7}H$^{7'}$ group in ^{3}III, these two protons should possess identical relaxation rates. Plots according to eq 17 showed this to hold not only for H^7 and H$^{7'}$ but also within experimental error for H^1, so the ratios of all three CIDNP signals were averaged to improve the precision.

As is evident from eq 17, the described evaluation is based on the deviations of the intensity ratios from the value in the absence of relaxation, −1, so a good signal-to-noise ratio is crucial. For these reasons, experiments on N could be evaluated

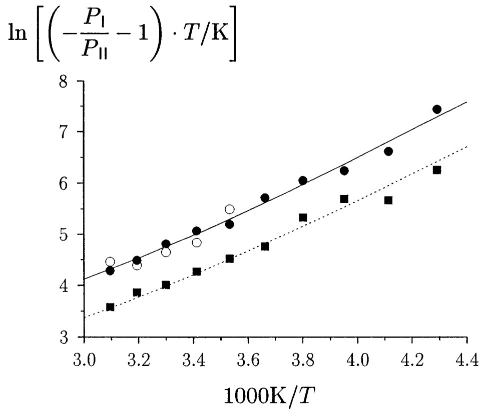


Figure 3. 3. Plots according to eq 17 for benzoquinone and quadricyclane in acetonitrile (●) and chloroform (■) and for benzoquinone and norbornadiene in acetonitrile (○). The solid regression line is for the first data set only, and the broken one, for the second. The slopes of the linear portions (see eq 17) of the two regression curves differ by less than 1 kJ/mol.

only in acetonitrile at temperatures above 280 K, whereas for Q, quantitative measurements down to 233 K were also possible in chloroform.

Intersystem crossing of ^{3}IV is not an activated process whereas ring closure of ^{3}III is, so in the limit of low and high temperatures, ln $\zeta(T)$ must approach ln 2 and $\ln(A/k''_{\mathrm{isc}}) - E_a/RT$, respectively. Equation 17 shows that in both cases $\ln[(-P_I/P_{II} - 1)T/\mathrm{K}]$ is a linear function of $1/T$. However, in the high-temperature limit, E_a would cancel, and the slope of the plots would be given by E_{vis}/R. The fact that the observed slopes in the linear fits are about three times as large as E_{vis}/R shows that our experimental conditions fall into the low-temperature regime.

This is also borne out by the product distribution. Applying the same simplifications as above ($k'_{\mathrm{op}} = k''_{\mathrm{op}} = k_{\mathrm{open}}$, $k'_{\mathrm{cl}} = k''_{\mathrm{cl}} = k_{\mathrm{close}}$) to eqs 13 and 14, one gets

$$\left(\frac{[\mathrm{II}]}{[\mathrm{I}]}\right)_{\mathrm{Q}} = \frac{1 + k_{\mathrm{close}}/k'_{\mathrm{isc}}}{1 + k_{\mathrm{close}}/k''_{\mathrm{isc}}} \tag{18}$$

$$\left(\frac{[\mathrm{II}]}{[\mathrm{I}]}\right)_{\mathrm{N}} = \frac{k''_{\mathrm{isc}}}{k_{\mathrm{close}}}\left(2 + \frac{k_{\mathrm{close}}}{k'_{\mathrm{isc}}}\right) \tag{19}$$

At 298 K, the product ratios $([\mathrm{II}]/[\mathrm{I}])_{\mathrm{Q}}$ and $([\mathrm{II}]/[\mathrm{I}])_{\mathrm{N}}$ are 2.9 ± 0.1 and 7.5 ± 0.2, respectively. Hence, at room temperature, $k_{\mathrm{close}}/k'_{\mathrm{isc}}$ is calculated to be 4.4 ± 0.4. By using this quantity, a very well-conditioned nonlinear fit of eq 17 to the data can be performed, the only adjustable parameters being E_a and an additive constant.

Evaluating the data of Figure 2 accordingly and using the value[10] of E_{vis} for the undeuterated solvent, one obtains an activation energy of 17 ± 2 kJ/mol with quadricyclane in acetonitrile. The influence of the term ln $\zeta(T)$ is seen to amount to less than 20%. Exactly the same result as with quadricyclane is expected for the quencher norbornadiene, and at those temperatures where the signal-to-noise ratio allowed quantitative evaluation, the data points are indeed seen to be describable by the same regression curve.

The ratios of the pertinent rate constants and the activation energy of the biradical rearrangement have been compiled in Table 1. It is seen that intersystem crossing is indeed significantly faster for ^{3}IV than for ^{3}III.

TABLE 1: Kinetic Parameters of the Cycloadditions[a]

$k_{\mathrm{close}}(298\ \mathrm{K})/k'_{\mathrm{isc}}$	E_a (kJ mol^{-1})	$k''_{\mathrm{isc}}/k'_{\mathrm{isc}}$
4.4 ± 0.4	17 ± 2	5.1 ± 0.2

[a] See text for further explanation.

Acetonitrile and chloroform possess an almost identical temperature dependence of the viscosity, E_{vis} differring only by about 1%, so it is not surprising that a very similar curve is also found for quadricyclane in chloroform. However, because chloroform has a slightly larger value of ln C than does acetonitrile, one would expect the curve to be shifted upward by about 0.4 units, the opposite of which is observed. Presumably, the small hydrodynamic effect is compensated by other factors such as slightly different spin density distributions in these two solvents of quite different polarity, with a concomitant change of d_{eff} (compare eq 16).

Evidently, ring closure of the norbornenyl moiety in ^{3}III to give the nortricyclyl intermediate ^{3}V is the rate-determining step of the interconversion of ^{3}III and ^{3}IV. The obtained activation energy is the lowest reported so far for a cyclopropylmethyl−homoallyl rearrangement. It amounts to only about two-thirds of that for ring closure of the unsubstituted norbornenyl radical (25 kJ mol^{-1})[13] and is about one-third of that for the trichloromethyl derivative (48 kJ mol^{-1}).[14] The observation[13] that oxygen substitution greatly stabilizes the nortricyclyl structure may provide a reason for the very low activation barrier in our system; besides, the large difference of E_a for the other two, very similar species also seems to indicate that slight structural and electronic effects strongly influence the rate of this rearrangement in the case of a norbornene skeleton.

Experimental Section

Norbornadiene and quadricyclane were distilled twice under nitrogen at reduced pressure; benzoquinone was purified by repeated sublimation under high vacuum. The deuterated solvents CD_3CN and $CDCl_3$ were dried with molecular sieves. Solutions of 8×10^{-3} M of the quinone and 1×10^{-2} M of the quencher were prepared under dry inert gas, deoxygenated by bubbling argon through them, and then sealed in NMR tubes.

The CIDNP experiments were performed with a slightly modified Bruker WM-250 spectrometer and a 308-nm excimer laser.[7] The method employed, pseudo-steady-state CIDNP measurements,[11] yields pure polarizations free from unchanging background signals.

CIDNP intensities were obtained from integrals over the respective signals after baseline correction of the spectra.

References and Notes

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