

# Photocycloadditions of Quinones with Quadricyclane and Norbornadiene. A Mechanistic Study

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**Abstract:** The photocycloadditions of *p*-quinones with quadricyclane (**Q**) and norbornadiene (**N**) to give oxolanes **I** and oxetanes **II** were investigated by measurements of chemically induced dynamic nuclear polarization (CIDNP) and NMR analysis of the products. With systems such as 1,4-benzoquinone/**Q** strong S–T<sub>0</sub>-type CIDNP was observed. The polarizations of the starting materials and of the rearranged hydrocarbon **N** are exclusively generated in radical ion pairs (RIPs) whereas the product polarizations predominantly stem from biradicals **III**. Both cycloadducts are formed by geminate processes, **I** resulting from the singlet exit channel of **III**, and **II** from the triplet exit channel. **III** was identified as a 1,5-biradical possessing the same structure as the oxolane **I** but with the C–C bond between the quinone and the norbornene moiety broken. A 1,2-shift of a vinyl group converts **III** into a 1,4-biradical **IV** also comprising a norbornenyl substructure, which is the direct precursor to **II**. This rearrangement occurs via a further 1,5-biradical **V** with a nortricycyl skeleton. Neither **IV** nor **V** give rise to CIDNP, which is explained by a smaller distance between the radical centers and a shorter lifetime compared to **III**. The reversible rearrangement **III** ⇌ **IV** does not depend on the electron spin multiplicity; in combination with the ability of **IV** to act as a chemical sink this provides the analogue to an escape reaction of radical pair CIDNP. By the competition of this “escape” process with nuclear-spin selective intersystem crossing S–T<sub>0</sub>-type CIDNP is generated in biradical **III**. Such a spin-sorting mechanism has been observed for the first time in this work. Superimposed on the biradical polarizations in the cycloadducts there are also polarizations stemming from RIPs. The relative amount of these two contributions strongly depends on the sensitizer and the quencher. From an analysis of these results and thermodynamic considerations it was inferred that electron transfer quenching precedes biradical formation whenever this is energetically feasible.

Photoinduced interconversion of norbornadiene **N** and quadricyclane **Q** is of considerable interest because of its potential use for solar energy storage.<sup>1</sup> The energy surfaces of these systems have been extensively studied for the excited singlet and triplet states<sup>1</sup> as well as radical cations<sup>2</sup> and anions.<sup>3</sup> Ketones and quinones are frequently employed as triplet sensitizers for the valence isomerizations of these strained hydrocarbons. Photocycloadditions of such carbonyl compounds<sup>4–9</sup>

to **N** or **Q** are unwanted side reactions that are obviously of great importance with respect to technical applications; it has also been proposed<sup>9</sup> that these processes provide a further isomerization pathway for **N** and **Q**. Yet, so far there have been but few<sup>8,9</sup> investigations of the mechanism of these reactions, all of which were concerned with quenching rates, quantum yields, and product distributions only, i.e. exclusively focussed on the reactants and the products. Neither direct nor indirect detection of the intermediates has been reported to date. In this paper, we study photoinduced oxetane and oxolane formation from *p*-quinones and **Q** and **N** by using measurements of chemically induced dynamic nuclear polarizations (CIDNP).<sup>10</sup>

CIDNP experiments are one of the most versatile methods for the investigation of radical and biradical reactions in solution. The CIDNP effect is either caused by nuclear spin selective intersystem crossing (S–T<sub>0</sub> mixing) or by electron-nuclear spin flips (S–T<sub>-1</sub> or S–T<sub>+1</sub> mixing), both processes taking place in the paramagnetic intermediates. This leads to nonequilibrium populations of the nuclear spin states of the diamagnetic reaction products, which manifest themselves as anomalous line intensities (enhanced absorption or emission) in NMR spectra recorded during the reactions. The attractiveness of CIDNP stems from the fact that mechanistic information of many different kinds is obtained by these measurements, which is especially valuable in the case of complex reactions. The products are monitored and can be characterized quite well, since detection is ac-

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complished by high-resolution NMR. For S-T<sub>0</sub>-type CIDNP, signs and magnitudes of the polarizations of different protons in the products reflect signs and magnitudes of the hyperfine coupling constants of these protons in the paramagnetic intermediates, thereby allowing identification<sup>11</sup> of the latter as well. The precursor multiplicity and the exit channel leading to a particular product can also be obtained from the polarization phases. Lastly, geminate and random phase processes can be distinguished by time-resolved CIDNP experiments.<sup>12</sup>

Our results establish that in the cycloadditions of both quadricyclane and norbornadiene with quinones a 1,5-biradical is a key intermediate with respect to CIDNP. This species provides one of the very rare examples<sup>13-16</sup> of S-T<sub>0</sub>-type CIDNP arising in a short-chain biradical. As we will show, for our systems a detailed profile of the reaction is obtained by CIDNP measurements.

## Results

**CIDNP Net Effects in the 1,4-Benzoquinone/Quadricyclane System.** Irradiation ( $\lambda = 308$  nm) of a solution of quadricyclane (**Q**) and 1,4-benzoquinone (**B**) in acetonitrile leads to strong CIDNP effects, as shown in Figure 1, bottom trace. Apart from the polarized resonances of the starting compounds, a multitude of new signals is seen in the CIDNP spectrum. By combining the CIDNP detection with decoupling and coherence-transfer experiments<sup>17</sup> it could be established that these signals belong to two reaction products only. As both were found to be stable under the experimental conditions, their unambiguous identification was possible by two-dimensional NMR spectroscopy; this was done on a mixture of the two products obtained by chromatography of a sample following prolonged irradiation at  $\lambda > 300$  nm. The structural formulas<sup>19</sup> of these compounds, an oxolane **I** and an oxetane **II**, are displayed in Figure 1. An assignment of the CIDNP signals is also given in the figure. The <sup>1</sup>H- and <sup>13</sup>C-NMR parameters of **I** and **II** are listed as supporting information, together with other NMR evidence for their structures. Formation of **I** and **II** in a ratio of approximately 1:1 from **Q** and **B** in benzene has been reported before.<sup>6</sup> However, from NMR spectra of our samples taken after illumination we obtained a lower ratio (about 1:3).

After identification of the reaction products—in which the polarizations are detected—the logical next step is to turn to the stage at which the polarizations arise. Interrelated issues are what intermediates the polarizations stem from, by which mechanism (S-T<sub>0</sub> or S-T<sub>±1</sub> mixing) they are generated, and what the multiplicities of the reacting species are. Information about this complex of questions can be obtained from the polarization patterns (the relative polarization intensities and phases of the different protons in the products) and from the absolute CIDNP phases.

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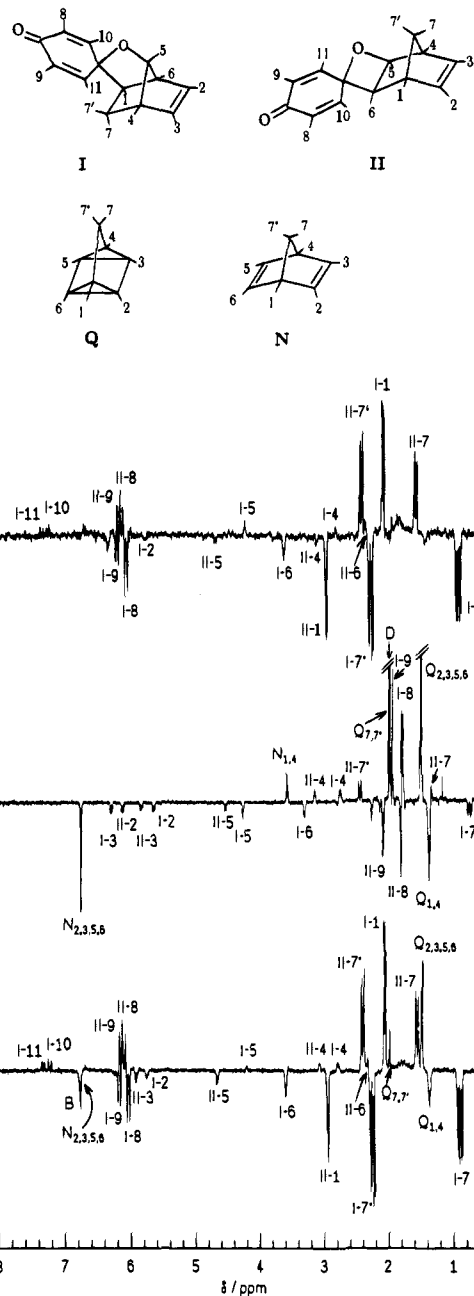
(15) Kaptein, R.; deKanter, F. J. J.; Rist, G. H. *J. Chem. Soc., Chem. Commun.* **1981**, 499–501.

(16) deKanter, F. J. J.; Kaptein, R. *J. Am. Chem. Soc.* **1982**, *104*, 4759–4766.

(17) Goetz, M. *J. Magn. Reson. A* **1993**, *102*, 144–150.

(18) As will be discussed below, norbornadiene **N** yields the same photoproducts as **Q**. To facilitate a comparison of these reactions, we therefore adopt the numbering of the protons in **N** for **Q** as well.

(19) The nonstandard numbering of the protons in the norbornene moieties of **I** and **II** has been chosen to emphasize the correspondence between them and their relation with the protons of the starting materials (see preceding Note and Discussion).



**Figure 1.** Background-free pseudo-steady-state CIDNP spectra obtained in the photoreaction of 1,4-benzoquinone (**B**) with quadricyclane (**Q**) (bottom trace, 16 scans), duroquinone with **Q** (center trace, 128 scans), and **B** with norbornadiene (**N**) (top trace, 64 scans) in acetonitrile-*d*<sub>3</sub> at room temperature. The assignment of the resonances of **Q** and **N** as well as of the products **I** and **II** refers to the structural formulas given at the top. For clarity, protons are designated by their numbers only; see refs 18 and 19 for the numbering. The signal of the benzoquinone protons is marked by **B** and that of the duroquinone protons by **D**. The methyl peaks of the products **I** and **II** formed in the reaction with duroquinone are denoted with the same numbers as the corresponding protons in the other spectra.

For the regenerated hydrocarbon **Q**, the same polarization pattern (strong emission for the protons **Q**<sub>1,4</sub> at the bridgehead positions, strong absorption for the protons **Q**<sub>2,3,5,6</sub> at the four-membered ring, and medium absorption for the protons **Q**<sub>7,7'</sub> of the methylene bridge) is observed as is found<sup>2</sup> in the photoreaction with 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil), where no adduct formation takes place. This pattern indicates<sup>2</sup> that the educt polarizations originate from intermediate radical ion pairs consisting of the benzoquinone radical anion **B**<sup>•-</sup> and the radical cation **Q**<sup>•+</sup> of quadricyclane.

Kaptein's rule<sup>10,20</sup> for a CIDNP net effect of proton  $i$

$$\Gamma_i = \mu \times \epsilon \times \text{sgn } \Delta g \times \text{sgn } a_i \quad (1)$$

relates its polarization phase ( $\Gamma_i = +1$ , absorption;  $\Gamma_i = -1$ , emission) to the precursor multiplicity  $\mu$  ( $\mu = +1$ , triplet or random phase;  $\mu = -1$ , singlet), exit channel<sup>21</sup> leading to the product observed ( $\epsilon = +1$ , product formation from the singlet state;  $\epsilon = -1$ , from the triplet state), sign  $\text{sgn } a_i$  of the hyperfine coupling constant of the proton considered, and sign of the difference of the  $g$ -values of radicals 1 and 2, where radical 1 contains the proton  $i$ . We must have  $\mu = +1$ , since the singlet state of **B** is too short-lived<sup>24</sup> to be quenched by the concentrations of **Q** used in our experiments. The  $g$ -value of **B**<sup>•-</sup> is 2.0050<sup>25</sup> while that of **Q**<sup>•+</sup> is 2.0035;<sup>26</sup> the proton hyperfine coupling constants in **B**<sup>•-</sup> are negative.<sup>27</sup> The emission signal of the protons of the regenerated quinone ( $\epsilon = +1$ ) is thus consistent with generation of the educt polarizations in radical ion pairs.

With chloranil, CIDNP is further observed<sup>2</sup> for the protons of the rearranged hydrocarbon norbornadiene (**N**), which show exactly opposite polarizations to those of the corresponding protons in **Q**. This effect is difficult to detect in Figure 1, since the signals  $N_{1,4}$  of the bridgehead protons are obscured by the peak I-6, the resonances  $N_{2,3,5,6}$  of the olefinic protons in **N** almost coincide with those of **B**, and the signals of the protons  $N_{7,7'}$  of the methylene bridge are too weak to be discernible. With other sensitizers (see below) the coincidences are removed, and the signals of the former two types of protons in **N** become clearly visible. Their intensity pattern (absorption for the bridgehead protons, emission for the olefinic protons)<sup>2</sup> confirms that in our systems **N** also results from escaping radical cations **Q**<sup>•+</sup>, which isomerize outside the cage.

As regards the cycloadducts, the occurrence of CIDNP in both **I** and **II** shows that the reaction leading to these compounds must involve either radical pairs or biradicals. The polarizations of different protons in the same product are seen to have unequal phases. This can only be explained by  $S-T_0$  mixing, that is CIDNP generation by the interplay of Zeeman and hyperfine interactions;  $S-T_{-1}$  or  $S-T_{+1}$  mixing would produce the same polarization phases for all protons of a particular product.<sup>13</sup> Hence, interpretation of the intensity patterns by using Kaptein's rules<sup>10,20</sup> is permissible regardless of the actual nature of the intermediates.

By integration of the CIDNP signals it is found that the polarization patterns of **I** and **II** are mirror images of one

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(21) The original definition<sup>20</sup> of  $\epsilon$  ( $\epsilon = +1$ , geminate or cage product;  $\epsilon = -1$ , random phase or escape product) is often equivalent to the convention<sup>16,22</sup> adopted here, because in many cases a geminate reaction is only feasible in the singlet state. However, it is not generally valid. Examples for geminate recombination of triplet radical pairs to give an electronically excited product<sup>22</sup> or another triplet intermediate that undergoes intersystem crossing without CIDNP generation<sup>23</sup> are known. In reactions involving biradicals capable of  $S-T_0$  mixing, yet other violations of the original rule are possible.<sup>16</sup> For the present investigation, it is necessary to differentiate between the nature of the process leading to the product and the multiplicity of the reacting intermediate. Both are pertinent to the mechanism but only the latter decides the polarization phases. For a distinction of these two categories, we shall use the terms *mode of formation* of the product and *exit channel*<sup>16</sup> of the intermediate.

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another.<sup>19</sup> (Apparent deviations from this relationship with respect to very weak signals, as for instance I-4 and II-4, which both appear in absorption, are due to a secondary effect that will be explained below.) This is clear evidence that the two cycloadducts stem from different exit channels of the same intermediate.

The intensity pattern observed for **I** as well as **II** is quite unlike that of the educt. It is in agreement neither with the spin density distribution in **Q**<sup>•+</sup> nor with that of its valence isomer **N**<sup>•+</sup>, the radical cation of norbornadiene. In **Q**<sup>•+</sup>, the two bridgehead protons  $Q_{1,4}$  and the four protons  $Q_{2,3,5,6}$  at the cyclobutane ring are known to have significantly larger hyperfine coupling constants than the other two protons; experimentally<sup>26</sup>  $a_{Q_{1,4}} = (+)0.66$  mT,  $a_{Q_{2,3,5,6}} = (-)0.51$  mT, and  $a_{Q_{7,7'}} = (-)0.20$  mT (the signs are from *ab initio* calculations<sup>28</sup> and were also inferred from CIDNP experiments<sup>2</sup>). For **N**<sup>•+</sup>, the hyperfine coupling constant of the four olefinic protons  $N_{2,3,5,6}$  is largest by far ( $a_{N_{1,4}} = -0.049$  mT,  $a_{N_{2,3,5,6}} = -0.78$  mT,  $a_{N_{7,7'}} = +0.304$  mT).<sup>29</sup> Yet, inspection of Figure 1 shows that only three protons are strongly polarized in each product, and one of these possesses opposite phase as the other two. It is thus obvious that a second radical pair, or biradical, besides **Q**<sup>•+</sup>**B**<sup>•-</sup> must be involved, in which CIDNP is generated and from which formation of **I** and **II** takes place.

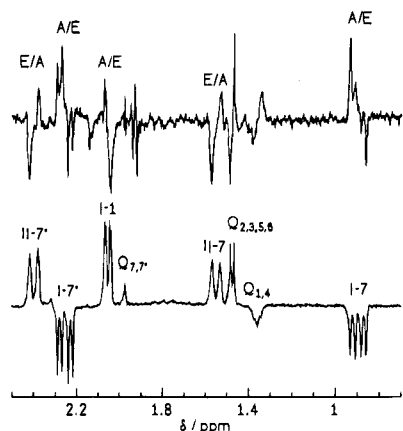
By comparing the signals of corresponding protons in the two cycloadducts it is finally seen that the CIDNP intensities in **II** are weaker by a factor of about 2 than those in **I**. As the nuclear spin sorting mechanism of  $S-T_0$ -type CIDNP produces opposite polarizations of exactly equal magnitude in the singlet and the triplet manifold of a radical pair or biradical, and as we have a single product from each exit channel of that intermediate, this can only be a manifestation of nuclear spin relaxation at the paramagnetic stage. For the same reason, the fact that the chemical yield of **II** is larger than that of **I** indicates that some fraction of the oxetane is formed without CIDNP generation. On the other hand, the strong polarizations exclude the possibility that only a very minor pathway via radical pairs or biradicals is responsible for the CIDNP signals of **I** and **II** whereas the reaction chiefly proceeds through other intermediates.

For clarity, we sum up the main results of the preceding analysis of CIDNP net effects in the system **B/Q** as follows. The polarizations of the starting materials and of the rearranged hydrocarbon **N** are in line with expectations based on earlier<sup>2</sup> work: They arise in radical ion pairs **Q**<sup>•+</sup>**B**<sup>•-</sup>, and isomerization of **Q** to give **N** takes place in free radical cations. The polarizations of the two cycloadducts, the oxolane **I** and the oxetane **II**, are also generated by  $S-T_0$  mixing. However, the source of these polarizations is not **Q**<sup>•+</sup>**B**<sup>•-</sup> but another paramagnetic intermediate, and **I** and **II** stem from different exit channels of this second radical pair, or biradical.

**Multiplet Effects.** With the information obtained so far, eq 1 does not allow unambiguous determination of the magnetic parameters  $\Delta g$  and  $\text{sgn } a_i$  of this second intermediate nor of the exit channels leading to **I** and **II**. With  $\mu$  known, however,  $\epsilon$  can be found if two protons  $i$  and  $j$  both display CIDNP net effects and a multiplet effect. As two such protons necessarily belong to the same product,  $\mu$  and  $\epsilon$  must be identical for them. For the relative phase  $\gamma_{ij}$  of their net polarizations

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**Figure 2.** Separation of CIDNP net and multiplet effects in the photoreaction of 1,4-benzoquinone with quadricyclane in acetonitrile- $d_3$ . Bottom trace, CIDNP net effects; top trace, CIDNP multiplet effects, amplitudes multiplied by 10. A/E and E/A denote the type of multiplet (cf. eq 3). The signals<sup>31</sup> have been assigned as in Figure 1. Only the region of the spectra containing the largest signals of the norbornene moiety in the products is shown.

we therefore have

$$\gamma_{ij} = \text{sgn } a_i \times \text{sgn } a_j \times \sigma_{ij} \quad (2)$$

where we assign  $\gamma_{ij} = +1$  to equal polarization phases of both protons, and  $\gamma_{ij} = -1$  to opposite phases. The parameter  $\sigma_{ij}$  takes into account whether the two protons were contained in the same radical of the intermediate pairs ( $\sigma_{ij} = +1$ ) or in different radicals ( $\sigma_{ij} = -1$ ). For a biradical, these cases would correspond to both protons experiencing hyperfine interactions predominantly with the same of the two radical centers or with different centers. The factor  $\sigma_{ij}$  enters eq 2 because of the term  $\text{sgn } \Delta g$  in the expression for CIDNP net effects, eq 1. According to Kaptein's rule<sup>10,20</sup> for a multiplet effect of protons  $i$  and  $j$ , the polarization phases  $\Gamma_{ij}$  are given by

$$\Gamma_{ij} = \mu \times \epsilon \times \text{sgn } a_i \times \text{sgn } a_j \times \text{sgn } J_{ij} \times \sigma_{ij} \quad (3)$$

$\Gamma_{ij} = +1$  denotes an E/A multiplet, that is emission to low field and absorption to high field;  $\Gamma_{ij} = -1$  signifies an A/E multiplet.  $J_{ij}$  is the nuclear spin-spin coupling constant in the product. Hence, by combining eqs 2 and 3 and rearranging the result we get

$$\epsilon = \Gamma_{ij} \times \gamma_{ij} \times \mu \times \text{sgn } J_{ij} \quad (4)$$

Separation of net and multiplet effects was performed by their dependence<sup>30</sup> on the flip angle  $\vartheta$  of the observation pulse. Two spectra were acquired with  $\vartheta = 45^\circ$  and  $135^\circ$ , respectively. Addition of these spectra yields pure net effects (Figure 2, bottom trace), subtraction pure multiplet effects (top trace).<sup>30</sup> Compared to the net effects, the multiplet effects are seen to be quite small, which is evidence for a rather large difference of the  $g$ -values<sup>10</sup> of the two radicals, or radical centers.

The geminal coupling constant  $^2J_{77'}$  is negative, whereas the vicinal coupling constant  $^3J_{17}$  is positive.<sup>32</sup> The A/E patterns

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(31)  $Q_{1,4}$  and  $Q_{2,3,5,6}$  seem to appear as E/A multiplets, which would be inconsistent with the mechanistic conclusions of ref 2. However, we regard these two signals as artifacts that are caused by insufficient background suppression of the resonances of the starting compound **Q**. This problem does not arise with the signals of **I** and **II**, since the amount of photoproducts formed during our measurements is negligible.

(32) Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*; Academic Press: New York, 1988; pp 191–193.

observed for protons 1, 7, and 7' of **I** therefore show that the oxolane is formed via the singlet exit channel. Protons 7 and 7' in **II** display E/A multiplets, thus indicating a triplet species as precursor to the oxetane.<sup>33</sup> This is also consistent with the above-mentioned observation that nuclear spin relaxation at the paramagnetic stage causes the polarizations of **II** to be considerably smaller than those of **I**.

**Solvent Dependence.** The unknown radical, or radical moiety, **R**<sup>•</sup> derived from **Q** can only be a hydrocarbon radical. Therefore, its  $g$ -value will not differ much from that of the free electron; certainly,  $g$  should be<sup>35</sup> smaller than 2.0030. In contrast, the radical, or radical center, resulting from **B** is expected to have some unpaired spin density at oxygen, so its  $g$ -value will be appreciably higher (for example, the neutral semiquinone radical **HB**<sup>•</sup> has<sup>36</sup>  $g = 2.0049$ , which is almost as large as the value for **B**<sup>•-</sup>). This is also consistent with the substantial  $g$ -value difference inferred from the observed small amplitudes of CIDNP multiplet effects. For the protons of the norbornene moiety in the products,  $\Delta g$  must thus be negative, so from the phases of the CIDNP net effects we find that the largest hyperfine coupling constant in **R**<sup>•</sup> is positive. This again excludes the radical cation **N**<sup>•+</sup>.

The strongest evidence against origination of the strong product polarizations in radical ion pairs such as **Q**<sup>•+</sup>**B**<sup>•-</sup> in general is obtained from experiments in nonpolar solvents. CIDNP can only be generated if the radicals constituting such a pair are able to separate to a distance where the exchange interaction between them becomes comparable to the S-T<sub>0</sub> mixing matrix element, which is determined by the Zeeman and hyperfine interactions. If the relative permittivity  $\epsilon_r$  of the solvent decreases, separation of oppositely charged radical ions becomes increasingly difficult and CIDNP is more and more suppressed. This effect has been verified experimentally.<sup>37</sup> In contrast, the diffusional dynamics of uncharged radical pairs or biradicals is left unchanged by the solvent polarity. As Figure 3 shows, with our system essentially equal—the very slight systematic differences as for instance the inversion of the signal II-4 will be discussed below—product polarizations are found in acetonitrile ( $\epsilon_r = 36$ ) and chloroform ( $\epsilon_r = 4.7$ ), apart from a reduction of the overall signal intensity by a factor of about 2 in the latter case. However, the CIDNP signals of the regenerated starting hydrocarbon **Q**, which stem from radical ion pairs, are totally absent in the less polar solvent. The same behavior is observed in benzene ( $\epsilon_r = 2.3$ ). It is thus

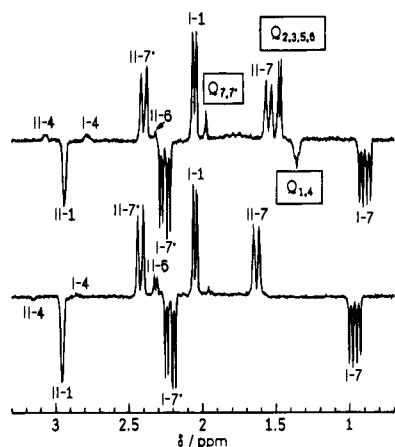
(33) As a referee pointed out, evaluation of small multiplet effects in the presence of large net effects may lead to wrong conclusions: Deviations from eq 3 have been found for higher fields or  $g$ -value differences.<sup>34</sup> So far, however, such behavior has only been observed in systems containing both <sup>1</sup>H and <sup>13</sup>C nuclei. To test for this source of errors, we simulated the signals of Figure 2 on which our assignment of  $\epsilon$  is based; for the calculations we used the hyperfine coupling constants compiled in Chart 1. Simulations were first performed with the simple method of ref 34c and considering protons 1, 7, and 7' only. For  $|\Delta g| \geq 0.0009$ , this indeed gave the opposite phases of CIDNP multiplet effects as predicted by eq 3. We then carried out simulations with a more recent reencounter model (Vollenwelder, J.-K.; Fischer, H. *Chem. Phys.* **1988**, *124*, 333–345) and took into account all the hyperfine coupling constants. Up to  $|\Delta g| = 0.003$ , this led to the same multiplet phases as eq 3. This seems to provide a *posteriori* justification that the simple sign rule does not fail for our systems, and we take this result to imply that our assignment of  $\epsilon$ —which is consistent with all the other experimental findings—is correct.

(34) (a) Salikhov, K. A. *Chem. Phys.* **1982**, *64*, 371–379. (b) Hore, P. J.; Stob, S.; Kemmink, J.; Kaptein, R. *Chem. Phys. Lett.* **1983**, *98*, 409–413. (c) Hutton, R. S.; Roth, H. D.; Bertz, S. H. *J. Am. Chem. Soc.* **1983**, *105*, 6371–6377. (d) Roth, H. D.; Hutton, R. S.; Hwang, K.-C.; Turro, N. J.; Welsh, K. M. *J. Phys. Chem.* **1989**, *93*, 5697–5701.

(35) Lawler, R. G. In ref 10a; pp 17–28.

(36) Maruyama, K.; Kato, H. *M. Fac. Sci., Kyoto Univ., Ser. Phys., Astrophys., Geophys. Chem.* **1985**, *36*, 463–480.

(37) Aizawa, T.; Sakata, T.; Itoh, S.; Maeda, K.; Azumi, T. *Chem. Phys. Lett.* **1992**, *195*, 16–20.



**Figure 3.** Photoreaction of 1,4-benzoquinone with quadricyclane in different aprotic solvents. CIDNP spectrum in  $\text{CDCl}_3$  (bottom) and in  $\text{CD}_3\text{CN}$  (top). The experimental parameters were identical in both measurements. Only a part of the aliphatic region is shown. The assignment of the resonances refers to the structural formulas in Figure 1.

unambiguously established that the predominant polarizations of **I** and **II** do not arise in radical ion pairs.

**Time-Resolved CIDNP Measurements.** The mode of formation of **II** is not decided by the triplet exit channel leading to it.<sup>21</sup> If a biradical were involved as the intermediate responsible for CIDNP, either an intermolecular<sup>38</sup> (random phase process) or an intramolecular (geminate reaction) chemical transformation in the triplet state may produce a secondary species that is the precursor to the oxetane. Examples<sup>39,40</sup> of both types of processes in biradical CIDNP or CIDNP in systems with restricted diffusion, respectively, have been reported. For radical pairs of triplet multiplicity, the oxetane may be the result of escape of the radicals from the cage and subsequent reactions of the resulting free radicals. This is the most common mode of product formation via the triplet exit channel of radical pairs. Another possibility would be cage recombination of triplet pairs to give a further triplet intermediate, which then decays to **II**. The latter mechanistic alternative is realized in other cycloadditions leading to oxetanes,<sup>23</sup> where correlated radical ion pairs in a triplet state yield a Paterno–Büchi biradical, which undergoes rapid intersystem crossing to the singlet state followed by ring closure.

Cage recombination of radical pairs takes place within a few nanoseconds, and the geminate life of a biradical typically also falls within this range.<sup>41</sup> In contrast, the reactions of escaping radicals cannot proceed faster than the diffusion controlled limit. For low radical concentrations, product formation thus takes place on a microsecond to millisecond time scale. Hence, geminate and escape pathways can be distinguished by time-resolved CIDNP experiments<sup>12</sup> ("flash-CIDNP"), although so far this seems to have been applied only to radical pair reactions.<sup>42</sup>

In flash-CIDNP experiments at room temperature, we could

(38) In the system **B/Q**, when no scavenger is added, an intermolecular reaction of a biradical could only occur with the starting materials or the solvent. However, such a reaction, especially with the strained hydrocarbon **Q**, cannot be excluded *a priori*. The same consideration applies to stabilization of a hypothetical radical intermediate by interaction with **Q**.

(39) (a) deKanter, F. J. J.; Sagdeev, R. Z.; Kaptein, R. *Chem. Phys. Lett.* **1978**, *58*, 340–345. (b) Turro, N. J.; Hwang, K.-C.; Rao, V. P.; Doubleday, C., Jr. *J. Phys. Chem.* **1991**, *95*, 1872–1879. (c) Hwang, K.-C.; Turro, N. J.; Doubleday, C., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 2850–2853.

(40) Hutton, R. S.; Roth, H. D.; Kraeutler, B.; Cherry, W. R.; Turro, N. J. *J. Am. Chem. Soc.* **1979**, *101*, 2227–2228.

(41) Caldwell, R. A. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum Press: New York, 1990; pp 77–116.

not detect any difference in the rates of formation of **I** and **II**. However, we did observe a small time dependence, all product signals reaching their final values within 200 ns. The maximum concentration of intermediates in these measurements was calculated to be  $2 \times 10^{-5}$  M from the amount of light absorbed in the active volume of the sample. According to the Smoluchowski equation, the rate constant of a diffusion controlled reaction should be below  $2 \times 10^{10}$   $\text{M}^{-1} \text{s}^{-1}$  under these circumstances. With this, we estimate a first half-life of more than 2  $\mu\text{s}$  for a bimolecular reaction of two radicals in the worst case. Such a lag between formation of **I** and **II** would be easily detectable with our flash-CIDNP apparatus (limiting time resolution 100 ns). We take the absence of this effect to indicate that the oxetane is not formed by escape from the cage. Both **I** and **II** are therefore geminate products. Given the almost instantaneous appearance of the product polarizations on the time scale of our measurements, we can furthermore rule out a major participation of random phase precursors. Thus, free radicals do not play a significant role in this reaction.

Cross relaxation in the diamagnetic reaction products may distort the signal intensities<sup>43</sup> and thus give rise to misleading polarization patterns. Compared with conventional CIDNP experiments, which are performed with continuous illumination, this effect should be considerably less important in our pseudo-steady-state measurements, where gated illumination is applied for 200 ms, and where the polarizations thus only persist for an average time  $\tau$  of 100 ms before they are sampled. Nevertheless, during  $\tau$  some amount of magnetization could still be transferred from the strongly polarization protons 1, 7, and 7' to other protons in their spatial vicinity and might obscure the weak genuine CIDNP signals of the latter nuclei. To test for this source of errors, we recorded a time-resolved CIDNP spectrum without intervening delay between laser flash and acquisition pulse, i.e. with  $\tau$  being zero. We observed the same CIDNP phases and relative intensities in this experiment as in the measurement of Figure 1. Hence, we conclude that for the systems investigated the polarization patterns in the spectra acquired with the pseudo-steady-state technique are undisturbed by cross relaxation.

#### Scavenging Experiments and Concentration Variation.

Although the time-resolved CIDNP experiments rule out an involvement of free radicals in the reaction, biradicals or radicals belonging to correlated pairs might still react with scavengers present in fairly high concentrations. However, experiments with singlet scavengers were inconclusive. In neat  $\text{CDCl}_3$ , absolute polarizations of **I** and **II** were decreased by some 50% in comparison to acetonitrile, as mentioned above, but no new products could be found. Addition of 0.1 M tributyltin hydride to solutions of the quinone and **Q** in acetonitrile- $d_3$  or  $\text{CDCl}_3$  also led to a reduction of the overall CIDNP intensities, which was most likely caused by direct reaction of the scavenger with the excited quinone, but did not produce any new signals. A further increase of the tributyltin hydride concentration was not feasible because of formation of two phases. Likewise, the only effect of adding 2 M  $\text{CD}_3\text{OD}$  to the solutions was a strong

(42) An intermolecular reaction of a biradical, i.e. a scavenging process, leads to a radical pair of the same multiplicity as the biradical provided that a singlet scavenger is employed. Usually, for lifetime reasons the triplet state of the biradical is scavenged, so a triplet pair is produced in which the radicals bear the nuclear spin polarizations from the triplet exit channel of the biradical. Subsequent transfer of these polarizations to the escape products of the radical pair proceeds on the time scale of free radical reactions. While an analysis of the polarization patterns might be difficult owing to a superposition of biradical and radical pair CIDNP, the mere fact that there is a time dependence on that time scale indicates that there must have been an escape reaction of the biradical.

(43) Closs, G. L.; Czeropski, M. S. *Chem. Phys. Lett.* **1977**, *45*, 115–116.

decrease of all polarizations; no evidence for incorporation of deuterium into **I** and **II** could be detected in the CIDNP spectra.

To test also for possible interactions of the intermediate with the starting materials,<sup>38</sup> we varied the quencher concentration within a factor of 20 ( $5 \times 10^{-3} \text{ M} < [\text{Q}] < 1 \times 10^{-1} \text{ M}$ ). All observed intensity effects could be attributed to the quenching efficiency. In particular, the ratio of CIDNP signals of the products and of regenerated **Q** remained constant, despite the fact that the polarizations of the educt stem from radical ion pairs  $\text{Q}^+\text{B}^-$  and those of **I** and **II** from another intermediate. Likewise, a variation of the sensitizer concentration ( $4 \times 10^{-3} \text{ M} < [\text{B}] < 1.6 \times 10^{-2} \text{ M}$ ; a larger range was impracticable owing to the accompanying change of the absorbance of the samples) did not produce any unexpected results.

In contrast, the presence of a triplet scavenger, oxygen, has a significant effect on the reaction. When acetonitrile solutions of **B** and **Q** were saturated with  $\text{O}_2$  at room temperature, absolute CIDNP intensities of regenerated **Q** remained nearly constant (about 20% reduction), indicating negligible additional quenching of the sensitizer triplet. However, the strongest product polarizations (of  $\text{H}^7$  and  $\text{H}^{7'}$ ) were decreased by a factor of more than 20 under these circumstances, and a few weak new signals appeared which we did not assign. This must mean that a triplet biradical is involved in the reaction leading to **I** and **II**. Unless this biradical were only a precursor to a pair of neutral radicals, which from a chemical point of view appears almost inconceivable, the results presented so far can only be explained if the product polarizations are generated by  $\text{S}-\text{T}_0$  mixing in this biradical. A lifetime of triplet biradicals exceeding 1 ns has been reported<sup>44</sup> as a prerequisite for oxygen trapping. On the one hand, this is comparable to the time scale of  $\text{S}-\text{T}_0$  mixing, especially in the high field (5.9 T) of our NMR spectrometer, so this mechanism does not appear impossible. On the other hand, our observation of product formation within 200 ns is thus consistent with the success of the oxygen-trapping experiment.

These findings indicate that with respect to CIDNP the key intermediate of this reaction is a biradical, and that both products are formed by geminate processes of this species despite their different exit channels.

The decrease of the product polarizations in the oxygen-scavenging experiments is accompanied by a change of the CIDNP patterns. For the oxolane, only the relative intensities of the most strongly polarized resonances I-7, I-7', and I-1 remain nearly unaffected. The emissive peaks I-2, I-3, and I-6 become much larger (by a factor of at least 4) in comparison to the former group of signals, I-3 for instance being invisible in the spectrum of Figure 1, bottom trace, but clearly discernible in the oxygen-scavenging experiment despite the substantial reduction of the overall intensities. Likewise, the absorptive resonance I-4 is found to be anomalously large. In contrast, I-8 and I-9, which were among the major signals in Figure 1, show much weaker polarizations than I-2 and I-6, the intensities now being comparable to I-10 and I-11. For I-5, even an inversion of phase is observed (absorption in the normal experiment, emission in the presence of oxygen). Yet, the changes are still more pronounced in the case of the oxetane. II-7 and II-7', which were the most conspicuous signals of that product in Figure 1, are absent in the scavenging experiment, II-2, II-3, II-5, and II-6 appear in emission, and II-1 as well as II-4 appear in absorption, all possessing about the same intensities. Absolute signal strengths of these resonances are

comparable to those of II-3 and II-4 in the normal CIDNP spectrum (Figure 1, bottom trace). II-8 to II-11 display somewhat weaker absorption. An explanation of these observations will be given in the next section, in connection with the results obtained by variation of the sensitizer.

**Other Sensitizers.** Photocycloaddition of **Q** to the sensitizers 2,6-dimethyl-1,4-benzoquinone, 1,4-naphthoquinone, 2-methyl-1,4-naphthoquinone (menadione), and 2,3,5,6-tetramethyl-1,4-benzoquinone (duroquinone) gave analogous products as with 1,4-benzoquinone. The polarization patterns found for the respective oxolane and oxetane were similar to those in Figure 1, bottom trace. However, the intensities of the product signals relative to  $\text{Q}_{2,3,5,6}$  decrease in the order of the sensitizers given. This trend is accompanied by an increase of the peaks  $\text{N}_{1,4}$  and  $\text{N}_{2,3,5,6}$ .

For the protons of the norbornene fragments in the cycloadditions one would expect relative net polarizations to be independent of the sensitizer because  $\Delta g$  is large<sup>10</sup> and the hydrocarbon-derived moieties of the intermediate biradicals must be identical in all these cases. However, close inspection of the spectra reveals subtle changes of the polarization patterns in the series from 1,4-benzoquinone to duroquinone. First, for different protons in the same product the ratios of net polarizations are not constant; for instance, the ratios I-1/I-7 and I-4/I-7 rise continuously in this series. Second, the ratios of polarizations of corresponding protons in **I** and **II** also change, e.g., II-4/I-4 becomes progressively larger while the opposite holds for II-7/I-7. Third, even inversions of polarization phases occur. I-5 shows absorption with 1,4-benzoquinone, is invisible with 2,6-dimethyl-1,4-benzoquinone, and is emissively polarized with the other three quinones (while II-5 is an emission peak of growing intensity throughout this series). The signals of protons 2 and 3 behave in a manner similar to proton 5: with 2,6-dimethyl-1,4-benzoquinone, only I-2 and II-3 are visible, both appearing in emission, but with the other sensitizers II-2 and I-3 also become observable and display emission as well. All the described anomalies are most pronounced in the CIDNP spectrum of duroquinone with **Q** in acetonitrile, which is shown in Figure 1, center trace.

In a nonpolar solvent (e.g.,  $\text{CDCl}_3$ ), the signal-to-noise ratio is lower than in acetonitrile. In addition, it becomes progressively poorer in the above series of sensitizers; in  $\text{CDCl}_3$  the system duroquinone/**Q** displays no CIDNP any more. However, in those instances where the small signals are yet detectable the intensity anomalies are found to be absent in that solvent. For example, with 1,4-naphthoquinone in  $\text{CDCl}_3$  the peaks of  $\text{H}^4$  and  $\text{H}^5$  are still clearly visible. They show absorption for the signal I-5 *vs* emission in acetonitrile and the reverse for II-4, while I-4 or II-5 have the same phases in both  $\text{CD}_3\text{CN}$  and  $\text{CDCl}_3$ . The inversion of the peak II-4 with the solvent can also be seen in the reaction with the sensitizer 1,4-benzoquinone (compare Figure 3).

While the first two anomalies could in principle be due to nuclear spin relaxation in the paramagnetic intermediates, the third anomaly cannot be explained at all in this way. Moreover, such an explanation would be contradicted by the fact that these effects do not occur in  $\text{CDCl}_3$ : As the hydrodynamic properties of chloroform and acetonitrile are very similar under our experimental conditions, rotational correlation times cannot differ much, and the interpretation of these observations by relaxation becomes untenable.

Equal polarization phases of a particular proton in **I** (singlet exit channel) and the corresponding proton in **II** (triplet channel), as found for  $\text{H}^2$ ,  $\text{H}^3$ ,  $\text{H}^4$ , and  $\text{H}^5$  in Figure 1 (center), seem to be at variance with  $\text{S}-\text{T}_0$  mixing. The most trivial explanation

(44) Adam, W.; Kilem, U.; Mosandl, T.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *J. Org. Chem.* **1988**, *53*, 4986-4992.

would be a wrong assignment, wrong in the sense that these protons were not identical in the intermediates but that, for instance, signals I-4 and II-5 as well as I-5 and II-4 belong together instead. Owing to the rearrangement possibilities of the norbornane skeleton, this hypothesis could not be disproved by simply regarding the positions of H<sup>4</sup> and H<sup>5</sup> in **I** and **II**. However, this reasoning could account neither for the variations of the polarization patterns with the sensitizer nor for the inversions of the peaks I-5 and II-4 with the solvent. In contrast, all the observed anomalies can be rationalized with a superposition of two kinds of signals: Polarizations of opposite phase in **I** and **II**, which derive from the biradical, must be overlaid by small polarizations of the same phase in both products. From a comparison of line intensities, it can be established that these extra polarizations are emissive for H<sup>2</sup>, H<sup>3</sup>, H<sup>5</sup>, and H<sup>6</sup>, absorptive for H<sup>1</sup> and H<sup>4</sup>, and emissive again, though of weaker intensity, for H<sup>7</sup> and H<sup>7'</sup>. Their origin cannot be S-T<sub>±1</sub> mixing because that would give rise to the same signal phase for all protons of a product.<sup>10</sup>

The additional CIDNP signals are obviously suppressed in a nonpolar solvent. Furthermore, they seem to be connected with the polarizations of the isomerized starting compound **N**, which stem from radical ion pairs: The growth of the norbornadiene peaks in the series from 1,4-benzoquinone to duroquinone is accompanied by an increase of the polarizations superimposed on the product signals, although relative to the signal Q<sub>2,3,5,6</sub> the latter increase is only weak. Lastly, their intensity pattern is in excellent agreement with the spin density distribution in Q<sup>•+</sup>. All these observations indicate that the additional polarizations are generated in radical ion pairs Q<sup>•+</sup>S<sup>•-</sup>, where S<sup>•-</sup> is the radical anion of the respective sensitizer. From the signal phases, they must be assigned to the triplet exit channel of these pairs.

The changes of the polarization patterns occurring during oxygen scavenging can be interpreted in a similar way. Obviously, the polarizations originating in the biradicals are strongly decreased in the presence of oxygen, as one would expect, but the polarizations stemming from the radical ion pairs are affected much less. Furthermore, from the intensity patterns observed in that experiment it is evident that the relative amounts of biradical and radical pair polarizations are different for **I** and **II** under these circumstances. The most pronounced signals of the oxolane, I-7 and I-7', belong to those protons that possess the strongest hyperfine coupling constants in the biradical and the weakest in the radical cation Q<sup>•+</sup>, so there must be some contribution of CIDNP from the former. However, the relative polarization intensities of the other protons in the norbornene moiety of **I**, which are comparable to those found in the system duroquinone/Q, point to a substantial involvement of radical ion pairs. This is supported by the polarization pattern of the quinone part. For these protons, CIDNP from the triplet exit channel of radical ion pairs is absorptive and of equal magnitude for all four protons. Hence, the polarizations generated in the radical ion pairs and in the biradicals oppose each other for I-8 and I-9, and have the same sign for I-10 and I-11, which can explain the relative intensities observed in the oxygen-scavenging experiment. In contrast, the polarization pattern of the hydrocarbon moiety of the oxetane is consistent with CIDNP originating predominantly from radical ion pairs. This is further corroborated by the equal phases and intensities of II-8 to II-11 found in the presence of oxygen. From the absolute intensities of the signals that are due to the norbornene part in **II** it must be concluded that the polarizations from the radical ion pairs possess about the same magnitudes in the oxygen-scavenging experiment as in the normal CIDNP experiment.

With other sensitizers possessing persubstituted benzoquinone fragments besides duroquinone, the described trends in the polarizations are carried to an extreme. The CIDNP signals with 2,3-dichloro-1,4-naphthoquinone as well as 9,10-anthraquinone exclusively stem from radical ion pairs. Only one addition product (the oxetane) is polarized, and the norbornadiene signals are very strong. With chloranil neither **I** nor **II** can be discerned. Only isomerization is observed, as was reported before.<sup>2</sup> The same holds for 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Lastly, we tested the sensitizers xanthone and benzophenone, the latter in particular having been employed in most of the mechanistic studies<sup>8,9</sup> of the photocycloadditions to norbornadiene and quadricyclane. However, these carbonyl compounds gave no CIDNP signals at all.

**Other Quenchers.** When the excited quinone is quenched with norbornadiene (**N**) instead of quadricyclane, **I** and **II** are also formed and display nuclear spin polarizations; as an example, the CIDNP spectrum obtained in the photoreaction of **B** with **N** is given at the top of Figure 1. No other addition products can be detected in this spectrum. Preparative photocycloaddition of **B** and **N** in benzene has been reported<sup>6</sup> to lead to **I**, **II**, a second oxolane, and a second oxetane isomer in a ratio of 1:3:1.3:0.9. In our case, spectra of the reaction mixture after irradiation gave a much higher content of **II** as well as of the other oxetane, the ratio being about 1:8:1:3. It is thus obvious that a considerable part of the products is formed without generation of nuclear spin polarizations.

As Figure 1 shows, practically identical intensity patterns of **I** and **II** are obtained with both hydrocarbons. It clearly follows that the same biradical is involved regardless of whether the starting compound is **Q** or **N**. Absolute CIDNP signal strengths are weaker by a factor of about 3 in the case of **N**, so the yield of the biradical must be correspondingly lower with the latter compound. However, this cannot be due to less efficient quenching of the benzoquinone triplet by **N** because the signal intensities remain unaffected if the concentration of **N** is increased. The existence of a common central intermediate in both reaction systems is in striking contrast to the reactions of **Q** and **N** via radical ion pairs:<sup>2</sup> There, two distinct radical cations, Q<sup>•+</sup> and N<sup>•+</sup>, exist with lifetimes exceeding the CIDNP time scale, i.e. a few nanoseconds. Both have different spin density distributions and thus give rise to different intensity patterns.

As shown in the preceding section, with the quencher **Q** in CD<sub>3</sub>CN both the regenerated hydrocarbon and its valence isomer **N** bear polarizations stemming from radical ion pairs; the same holds for the educt quinone. In contrast, no signals of the starting materials appear in those reactions with **N** that lead to cycloadducts (with the sensitizers 1,4-benzoquinone, 2,6-dimethyl-1,4-benzoquinone, and 1,4-naphthoquinone). This effect cannot be explained by the above-mentioned coincidences of the peaks N<sub>1,4</sub> and N<sub>2,3,5,6</sub> with other signals since it is not only found in the spectrum of the **B/N** system but also with the other quinones, where the norbornadiene resonances are well separated from the peaks of the sensitizer and the products. Likewise, with regard to **I** and **II** no polarizations from radical ion pairs are superimposed on the biradical polarizations: with **N**, the intensity patterns depend on neither the solvent nor the sensitizer, and they are identical to those observed with **Q** in CDCl<sub>3</sub>, in particular with respect to the small peaks (e.g., I-4 being in absorption and II-4 in emission, compare Figures 1, top, and 3). Hence, none of the CIDNP signals can be traced back to radical ion pairs in these systems. In contrast, the sensitizers chloranil and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone show

exactly the opposite behavior. With these, all polarizations stem from radical ion pairs and thus only arise in polar solvents, CIDNP is solely found for the starting hydrocarbon **N**, and no new products are formed.

Absolute CIDNP intensities were found to be significantly lower in all photocycloadditions with **N** than in the corresponding ones with **Q**. The signals are too weak to be detectable even with menadione in CD<sub>3</sub>CN or with 1,4-naphthoquinone in CDCl<sub>3</sub>.

To obtain further information about the mechanism of the cycloadditions, we studied the photoreaction of **B** with 7-methylnorbornadiene. Again, formation of an oxolane and an oxetane of structures **I** and **II** was observed, and the polarization patterns were quite similar to those encountered in the previous cases. Although the CIDNP signals were somewhat smaller than with the unsubstituted quencher, protons 1, 5, 6, 7, and 7' of both products were clearly visible in the spectra. In **I** as well as **II** the methyl group was found to occupy exclusively the 7-position (for the numbering see Figure 1). As no scrambling occurs, the reaction must proceed stereospecifically. The protons of the methyl groups were only weakly polarized.

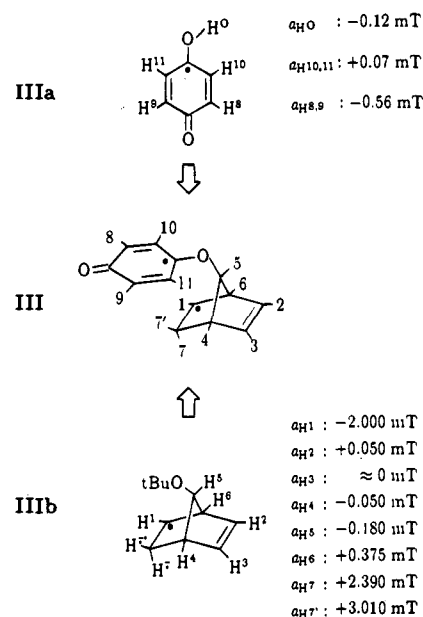
Finally, norbornene and tricyclene (1,1,7-trimethyltricyclo[2.2.1.0<sup>2,6</sup>]heptane) were used as quenchers to check whether the homoconjugated double bond or the second cyclopropane ring are prerequisites for CIDNP in these systems. No polarizations were found in the former case, and very weak polarizations in the latter that did not display any resemblance to those encountered with **N** or **Q**, both with regard to the NMR parameters of the photoproducts and to the intensity patterns. Hence, either of these two structural features is obviously essential for formation of the biradical intermediate giving rise to the polarizations.

## Discussion

**Structure of the Key Intermediate.** When radical pair CIDNP is employed in mechanistic research, one of the most valuable assets of this method is the possibility to identify the structure of the intermediates by an analysis of the intensity patterns in the products.<sup>11</sup> The basis for this is provided by the direct correspondence, with regard to both sign and magnitude, between net polarization  $P_i$  and hyperfine coupling constant  $a_i$  of proton  $i$ : If  $\Delta g$  is large,  $P_i$  and  $a_i$  are roughly proportional<sup>10</sup> to one another; the accuracy of this approximation improves with increasing interdiffusion coefficient.<sup>45</sup>

This relation is presumed to hold for S-T<sub>0</sub>-type CIDNP in biradicals as well, since the predominant contributions to the polarizations stem from configurations in which the two unpaired spins are farthest apart and the exchange integral  $J(r)$  is smallest in relation to the mixing matrix element. While absolute polarizations will be reduced by the non-negligible exchange interaction (an effect<sup>46</sup> that occurs also in radical pair CIDNP) to an extent depending on the unknown function  $J(r)$  and details of the molecular motions, evaluation of relative polarizations should thus still be reliable. In particular, owing to the restricted diffusion the durations between reencounters of the two radical centers are very short; in radical pair CIDNP, this would correspond to a system with extremely high interdiffusion coefficient, so the deviations from the proportionality between  $P_i$  and  $a_i$  are expected to be quite small. Hence, it seems permissible in our case to obtain, from the polarization patterns in the photoproducts, the spin density distributions of the quinone-based and hydrocarbon-based

## Chart 1



moieties separately, in the same way as for the two radicals of a correlated pair. Chart 1 illustrates this procedure.

For the quinone fragment we have  $\Delta g > 0$ . Considerable polarizations of H<sup>8</sup> and H<sup>9</sup> are observed (see Figure 1, bottom trace), which are practically equal if the superposition of the emissive and absorptive signals I-9 and II-9 is taken into account. In contrast, the polarizations of H<sup>10</sup> and H<sup>11</sup> are much weaker (by a factor of about 6 in **I**),<sup>47</sup> again approximately equal to each other, and have opposite phase to those of H<sup>8</sup> and H<sup>9</sup>. In the quinone moiety of the biradical, the two protons at the  $\beta$  positions relative to the carbon atom where the combination with the norbornene fragment occurs therefore possess a substantial positive hyperfine coupling constant, the other two ring protons a much weaker negative one. The pattern is in excellent agreement with the spin density distribution in the neutral benzosemiquinone radical **IIIa**. Its hyperfine coupling constants<sup>48</sup> are given in Chart 1, with the numbering of the protons as in our reaction products.

Since the lifetime of a singlet biradical is extremely short, it is reasonable to assume that the structure of the intermediate corresponds to the structure of the product formed via the singlet exit channel, the oxolane **I**. In connection with the identification of the quinone-based moiety this leads one to infer a 1,5-biradical of structure **III**, as shown in Chart 1. This is corroborated by the polarization patterns obtained for the hydrocarbon-derived radical moiety **R<sup>•</sup>**. Integration of the signals I-7', I-7, I-1, and I-6 yields  $a_{H^{7'}}:a_{H^7}:a_{H^1}:a_{H^6} \approx 100:86:-73:14$ . This pattern indicates that the unpaired electron in **R<sup>•</sup>** is localized at C<sup>1</sup>.  $\sigma$ - $\pi$  spin polarization serves to induce a negative spin density at H<sup>1</sup>, and hyperconjugation is responsible for the positive spin densities at the neighboring protons.<sup>49</sup> The noticeably larger value of  $a_{H^{7'}}$  than of  $a_{H^7}$  points to a larger

(47) In the spectrum of Figure 1, bottom trace, the signals of H<sup>10</sup> and H<sup>11</sup> in **II** seem to be missing. The effect is again due to a superposition of polarizations from radical ion pairs **Q<sup>•+</sup>B<sup>•-</sup>** via the triplet exit channel. Since we have  $\Delta g > 0$ ,  $\mu = +1$ ,  $\epsilon = -1$ ,  $a < 0$ , these polarizations are absorptive and compensate the emissive polarizations of H<sup>10</sup> and H<sup>11</sup> from the biradicals. However, in CDCl<sub>3</sub> the latter become clearly visible; in the spectrum of Figure 1, top trace, where they should likewise be observable, they are buried in noise.

(48) Meng, Q.-X.; Suzuki, K.; Maeda, K.; Terazima, M.; Azumi, T. J. Phys. Chem. **1993**, *97*, 1265-1269.

(49) Carrington, A.; McLachlan, A. D. *Introduction to Magnetic Resonance*; Harper & Row: New York, 1969; pp 80-85.

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(46) Burri, J.; Fischer, H. Chem. Phys. **1989**, *139*, 497-502.



overlap of the orbital accommodating the unpaired electron with the C–H<sup>7</sup> bond than with the C–H<sup>6</sup> bond, which is easily rationalized by H<sup>7</sup> and H<sup>7</sup> occupying axial and equatorial positions in a ring system, and by a slightly nonplanar structure around the carbon atom bearing H<sup>1</sup>. In contrast, the C–H<sup>6</sup> bond must be nearly orthogonal to that orbital.

The hyperfine coupling constants of the *tert*-butoxybicyclo[2.2.1]heptenyl radical **IIIb** have been determined.<sup>50</sup> They are compiled in Chart 1, adopting our numbering. For this radical, one has  $|a_{H^7}|:|a_{H^7}|:|a_{H^1}|:|a_{H^6}| \approx 100:79:66:12$ , which is in quite good agreement with the values obtained from the CIDNP signal intensities. Besides the hyperfine coupling constants of H<sup>1</sup>, H<sup>6</sup>, H<sup>7</sup>, and H<sup>7</sup>, three other coupling constants were measured in ref 50 but could not be assigned. By using the polarization patterns, it is possible to assign them consistently; their numerical values (from ref 50) and signs (from our CIDNP experiments) have also been included in the chart, and are seen to fit well with the observed polarization intensities. Likewise, with the EPR data the configuration of the substituent at the bridge could not be decided,<sup>50</sup> but from the CIDNP results the stereochemistry of **IIIb** shown in Chart 1 can be inferred. The direct correspondence between hyperfine coupling constants and polarization intensities of the most strongly polarized protons and the consistency that can be reached between the other EPR and CIDNP parameters substantiate that the spin density distribution in the hydrocarbon fragment of the biradical is very similar to that in **IIIb**.

Lastly, the CIDNP spectrum of the B/Q system (Figure 1, bottom trace) yields an intensity ratio I-8/I-7 of about 1:3.7 whereas the ratio of hyperfine coupling constants of the respective protons in **IIIa** and **IIIb** is 1:4.2. This is additional support that the biradical contains both these substructures. Considering *all* the CIDNP evidence, including the results of the time-resolved and scavenging experiments, one thus arrives at an intermediate of formula **III**.

We should like to point out that some of the experimental observations, e.g., the solvent dependence of the polarizations, would also be compatible with CIDNP generation in pairs of neutral radicals, and that the polarization patterns taken on their own might not have provided unequivocal evidence against these intermediates. Such pairs could be formed by hydrogen abstraction from **Q** or **N**, respectively, by the sensitizer triplet; this type of photoreaction of carbonyl compounds is ubiquitous with other quenchers, for instance amines.<sup>51</sup> This pathway has indeed been postulated<sup>52</sup> for other photoadditions of quinones to olefins. In the following, we will discuss the implications of such a cycloaddition mechanism via pairs of neutral radicals.

Obviously, hydrogen abstraction would produce the neutral benzosemiquinone radical **HB**<sup>•</sup> and thus give rise to the same polarization pattern of the quinone moieties as observed. **HB**<sup>•</sup> contains one additional proton, at oxygen. Its hyperfine coupling constant  $a_{H^0}$  is known<sup>48</sup> to be small and negative (see Chart 1). From the structure of **I** and **II** it is seen that this proton would have to be removed during product formation and presumably be taken up by the norbornene moiety. There, it would display the same CIDNP phase as a proton with a positive hyperfine coupling constant in **R**<sup>•</sup>, as follows from eq 1. However,  $a_{H^0}$  is much too small to account for the strong polarizations of H<sup>1</sup>, H<sup>7</sup>, or H<sup>7</sup> or even those of H<sup>6</sup>; based on the hyperfine coupling constants one would estimate a signal intensity of this proton that is only about twice that of H<sup>10</sup> or

H<sup>11</sup>. Besides, it is questionable whether this proton could acquire notable polarization at all, as it will exchange readily with the protons of residual water ( $\sim 5 \times 10^{-3}$  M under our experimental conditions). Owing to hydrogen bonding to the quinone, the water concentration in the vicinity of **HB**<sup>•</sup> should be significantly higher than the bulk concentration, so one would expect this exchange to occur efficiently also during the short life of the correlated radical pairs.

Removal of a proton from **Q** or **N** would yield a species C<sub>7</sub>H<sub>7</sub><sup>•</sup>, which from its sum formula is seen to contain four double bond or ring equivalents. With a norbornane or quadricyclane skeleton it is possible either to comply with this requirement or to account for the polarization pattern of **R**<sup>•</sup>, but not both at the same time, the argument running as follows. The norbornane skeleton contains two ring equivalents. Since the fragment –CH<sup>7</sup>H<sup>7</sup>–•CH<sup>1</sup>–H<sup>6</sup>C<, which is required by the polarization pattern observed, would already be part of the bicyclic structure, two other double bonds or rings would have to be formed involving the carbon atoms bearing H<sup>2</sup>, H<sup>3</sup>, H<sup>4</sup>, and H<sup>5</sup>. It is immediately obvious that this would lead to an extremely strained molecule containing two double bonds at bridgehead atoms, or three connected cyclopropane rings to give a pyramidal carbon, or a combination of both structural elements. Such a molecule can be excluded for energetic reasons. This dilemma might be resolved by taking into account dimers composed of the C<sub>7</sub>H<sub>7</sub><sup>•</sup> species and **Q** or **N**, which would give a nortricyclane radical bridged in such a way as to form an additional 5- or 6-membered ring, but the absence of any concentration dependence rules this out. On the other hand, the obvious position in **N** to abstract a hydrogen from would be the bridge. However, the resulting radical possesses one large hyperfine coupling constant only (for the remaining proton at the bridge), the others are negligible.<sup>53</sup> We expect a similar spin density distribution for the corresponding quadricyclane-based radical, by analogy with the nortricyclyl radical.<sup>50</sup> Thus, neither of these species qualifies as intermediate **R**<sup>•</sup>, since neither can give rise to the polarization pattern observed.

It is well known<sup>54</sup> that the quadricyclyl radical rapidly rearranges to the bicyclo[3.2.0]hepta-3,6-dien-2-yl radical, which represents a much more stable species on the C<sub>7</sub>H<sub>7</sub><sup>•</sup> hypersurface. Although this particular molecule is incompatible with the polarization pattern owing to its symmetry, two of its isomers, namely the 1,3-dien-6-yl and the 4,6-dien-2-yl radical, cannot be definitely excluded on the basis of the CIDNP spectra. The hyperfine coupling constants of these radicals were calculated by AM1. This procedure is not very accurate but the results agreed with expectations based on data for other cyclic alkyl radicals. The obtained values of  $a_{H^7}$ ,  $a_{H^7}$ ,  $a_{H^1}$ , and  $a_{H^6}$  were too similar to those computed for **IIIb** or those derived from the CIDNP experiments to be conclusive. While these species are not observed<sup>54</sup> in EPR experiments, they might nevertheless be formed on the CIDNP time scale (some nanoseconds for geminate processes) and give rise to polarizations. The energies of the 1,3-dien-6-yl and the 4,6-dien-2-yl radical (heats of formation calculated by AM1 495 and 525 kJ/mol) were estimated to be significantly higher than that of the 3,6-dien-2-yl isomer (418 kJ/mol), but AM1 indicates these species to be much more stable than the quadricyclyl radical (594 kJ/mol), which would be the primary result of hydrogen abstraction from **Q**. For the norbornadienyl radical, a value of 452 kJ/mol is obtained. Given the uncertainty of the AM1 results for our compounds,<sup>55</sup> formation of bicyclo[3.2.0]hepta-

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(53) Sugiyama, Y.; Kawamura, T.; Yonezawa, T. *J. Chem. Soc., Chem. Commun.* **1978**, 804–804.

(54) (a) Sugiyama, Y.; Kawamura, T.; Yonezawa, T. *J. Am. Chem. Soc.* **1978**, *100*, 6525–6526. (b) Sustmann, R.; Brandes, D.; Lange, F.; Nüchter, U. *Chem. Ber.* **1985**, *118*, 3500–3512 and references therein.

1,3-dien-2-yl from the norbornadienyl radical may thus still be feasible energetically.

However, apart from the oxygen-scavenging experiments, which corroborate the intermediacy of triplet biradicals and not of uncharged radical pairs, chemical considerations also rule out the latter intermediates. Combination of two radical centers will produce but one new bond; cycloaddition via correlated radical pairs therefore requires that a second bond be formed after geminate recombination. This can be realized if radical *ion* pairs combine, and examples of this type of reaction are indeed known,<sup>23</sup> but for pairs of neutral radicals this pathway is hardly conceivable. An alternative in this case would be if the resulting diamagnetic species contained two positions capable of reacting with each other or if a pericyclic reaction occurred as a secondary process. It seems doubtful whether the former could be achieved without side effects, because the structural elements allowing efficient ring closure of the radical combination product would have to be absent in the starting materials to prevent a reaction before radicals are generated, i.e. already in the dark. Although a pericyclic reaction might be formally possible, with our systems for instance if the hydrogen atom taken up by the quinone moiety would migrate to the hydrocarbon moiety by a sigmatropic rearrangement, this tends to be ruled out by thermodynamic considerations: The reaction would stop at the stage of the primary recombination product because as an open-chain compound this would almost certainly be lower in energy than the cycloaddition products comprising strained rings, and would invariably be favored entropically. On these grounds, a cycloaddition involving a pair of neutral radicals appears extremely unlikely *in general*, unless very unusual structural features are present.

In short, from the preceding analysis of the CIDNP results it must be concluded that the 1,5-biradical **III** shown in Chart 1 is the predominant source of the product polarizations in the systems **B/N** and **B/Q**. Despite their generation in a biradical, these polarizations originate from S-T<sub>0</sub> mixing, a mechanism that is usually restricted to radical-pair CIDNP.<sup>16,39b</sup> There are but very few precedents in the literature<sup>13-16</sup> of S-T<sub>0</sub>-type CIDNP arising in such a short-chain biradical.

**Thermodynamics of Oxetane Formation.** As the observed CIDNP net and multiplet effects show, the oxetane **II** results from the triplet exit channel of the biradical **III**. Formation of an electronically excited product, i.e. <sup>3</sup>**II**, seems to suggest itself as an explanation. To test this hypothesis, we investigated whether this reaction is thermodynamically feasible.

AM1 calculations gave a difference in the heats of formation  $\Delta H_f^\circ$  of the oxetane **II** and the starting materials **B** + **N** in their ground states of -11 kJ/mol (computed values of  $\Delta H_f^\circ$ : **B**, -105 kJ/mol; **N**, +283 kJ/mol; **II**, +167 kJ/mol). However, AM1 is not always sufficiently reliable for the compounds studied in this work (compare ref 55). For an independent check, we therefore resorted to group increments<sup>57</sup> to obtain the thermodynamical quantities, making use of measured heats of formation whenever available. The error expected with this method should certainly be very low. A further advantage of this procedure is that reaction entropies, which are by no means negligible in a cycloaddition since the number of species changes, may also

be estimated fairly reliably. Hence, thermodynamic arguments can be based on  $\Delta G^\circ$ , not  $\Delta H^\circ$ . In the following, we will use Benson's nomenclature<sup>57</sup> for the groups. The increments were taken from ref 57 except where noted.

The experimental heats of formation of **B** and of **N** are<sup>56</sup> -122.9 and +245.9 kJ/mol, respectively. The cyclohexadienone part of **II** contains the groups  $2 \times C_d-(H)(CO)$  (+20.9 kJ/mol each),  $2 \times C_d-(H)(C)$  (+35.9 kJ/mol each),  $1 \times (CO)-(C_d)_2$ , and  $1 \times C-(C_d)_2(C)(O)$ . For the group increment for the quinone carbonyl function, which is not tabulated, a value of -103.3 kJ/mol was obtained from the experimental<sup>56</sup>  $\Delta H_f^\circ$  of **B** and the increment for  $C_d-(H)(CO)$  given above. The value for  $C-(C_d)_2(C)(O)$  was approximated by taking that for  $C-(C)_3(O)$  (-27.6 kJ/mol) and adding 2.8 kJ/mol, the difference of the group increments for  $C-(C_d)_2(H)_2$  and  $C-(H)_2(C)_2$ . For the ring correction, we use the value for 1,4-cyclohexadiene (+2.1 kJ/mol). One carbon atom of the oxetane ring has already been taken into account when calculating the cyclohexadienone moiety. For the rest, we have  $1 \times O-(C)_2$  (-97.1 kJ/mol),  $1 \times C-(H)(C)_2(O)$  (-30.1 kJ/mol), and  $1 \times C-(H)(C)_3$  (-7.9 kJ/mol). Both 105.4 and 25.0 kJ/mol must be added for ring strain and for one *syn* interaction that is not present in the oxetane skeleton. Finally, for the norbornene part, we take the experimental heat of formation of that compound (+90.0 kJ/mol)<sup>56</sup> minus  $2 \times C-(H)_2(C)_2$  at -20.7 kJ/mol each, because these groups form part of the oxetane ring and were considered there. The total heat of formation of **II** is thus estimated to be +114 kJ/mol, 53 kJ/mol less than the value calculated by AM1. Hence, the ground state reaction **B** + **N**  $\rightleftharpoons$  **II** should be nearly thermoneutral ( $\Delta H^\circ = -9$  kJ/mol). The agreement of  $\Delta H^\circ$  with the AM1 result is extremely good; obviously, with the semiempirical method the substantial errors in the individual heats of formation cancel efficiently.

For the calculation of  $\Delta S^\circ$ , we utilize the fact that the connectivities, and thus the group increments, of large parts of the molecules remain unchanged in the reaction. As far as the hydrocarbon moiety is concerned, two groups  $C_d-(H)(C)$  (+33.3 JK<sup>-1</sup> mol<sup>-1</sup> each) are replaced by  $1 \times C-(H)(C)_3$  (-50.5 JK<sup>-1</sup> mol<sup>-1</sup>) plus  $1 \times C-(O)(C)_2(H)$  (-46.0 JK<sup>-1</sup> mol<sup>-1</sup>), and two groups  $C-(C_d)_2(C)(H)$  by  $2 \times C-(C_d)(C)_2(H)$ . We expect the entropy change in the latter case to be very small because the masses of the connected atoms do not change, and we approximate it by twice the difference between  $C-(C_d)_2(H)_2$  (+42.7 JK<sup>-1</sup> mol<sup>-1</sup>) and  $C-(C_d)(C)(H)_2$  (+41.0 JK<sup>-1</sup> mol<sup>-1</sup>). By the same token, in the quinone part two groups  $C_d-(H)(CO)$  become  $2 \times C_d-(H)(C)$  (+33.3 JK<sup>-1</sup> mol<sup>-1</sup>). As the increment for the former is unavailable, we use the value for  $C_d-(C_d)(H)$  (+26.7 JK<sup>-1</sup> mol<sup>-1</sup>) as a substitute, which should constitute a negligible error. In addition,  $(CO)-(C_d)_2$  changes into  $C-(C_d)_2(C)(O)$ . Owing to the lack of existing data, we replace the former by  $(CO)-(C)_2$  (+62.8 JK<sup>-1</sup> mol<sup>-1</sup>) and the latter by  $C-(O)(C)_3$  (-140.4 JK<sup>-1</sup> mol<sup>-1</sup>). It is assumed that the error caused by this approximation is quite small. The spiro carbon of the oxetane ring has already been taken into account in the quinone fragment, and the other two carbon atoms in the norbornene moiety. The remaining contributions are due to the group  $O-(C)_2$  (+36.3 JK<sup>-1</sup> mol<sup>-1</sup>) and the ring itself (+115.9 JK<sup>-1</sup> mol<sup>-1</sup>). Lastly, the loss of symmetry during the reaction must be considered. None of the molecules contains free rotors, so internal symmetry can be disregarded. External symmetry numbers are 4 for **B** and 2 for **N**, leading to an additional term  $+R(\ln 4 + \ln 2)$ . For the entropy of the reaction, we therefore get -187 JK<sup>-1</sup> mol<sup>-1</sup>. At room temperature, the entropy contribution to  $\Delta G^\circ$  is thus as high as +56 kJ/mol. This puts the oxetane in its ground state some 50 kJ/mol above the starting compounds, also in their ground states.

(55) AM1 overestimates the heats of formation of such strained hydrocarbons even in their ground states to a large and varying degree (norbornadiene: experimental,<sup>56</sup> 246 kJ/mol, AM1, 283 kJ/mol; quadricyclane: experimental,<sup>56</sup> 339 kJ/mol, AM1, 437 kJ/mol).

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(57) (a) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279-324. (b) Eigenmann, H. K.; Golden, D. M.; Benson, S. W. *J. Phys. Chem.* **1973**, *77*, 1687-1691.

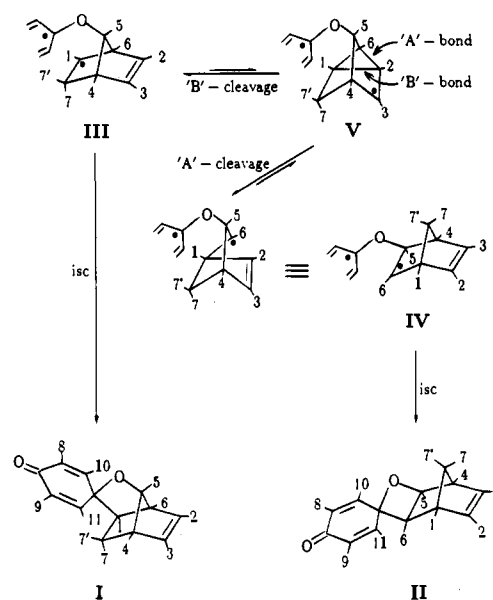
As a model compound for the oxetane triplet, we take 4-methyl-4-(trichloromethyl)-2,5-cyclohexadien-1-one. Its triplet energy  $E_T$  is<sup>58</sup> 280 kJ/mol. Replacement of trichloromethyl by the more electronegative OR group will decrease  $E_T$  slightly,<sup>58</sup> by an estimated 30 kJ/mol in the worst case. With  $E_T$  of **B** being 221 kJ/mol,<sup>59</sup> the free enthalpy of triplet quinone <sup>3</sup>**B** plus norbornadiene should thus be lower by at least 70 kJ/mol than that of the triplet oxetane <sup>3</sup>**II**. Hence, <sup>3</sup>**II** cannot be formed in this reaction. This argument does not make any assumptions about  $\Delta G^\circ$  for biradical formation from <sup>3</sup>**B** + **N**; however, this process is unlikely to be endergonic, otherwise quenching would not proceed efficiently, so the free enthalpy of the biradical is expected to be lower than that of <sup>3</sup>**B** + **N**.

On these grounds, we regard it as certain that a geminate reaction of the biradical **III** via the triplet exit channel to give an electronically excited oxetane <sup>3</sup>**II** is not feasible thermodynamically. Since exactly the same intermediate is involved in the photocycloaddition of **B** with norbornadiene as well as that with quadricyclane, this conclusion applies to both reaction systems.

**Pathways of Biradical Decay.** To identify the biradical **III**, we chiefly exploited the fact that the CIDNP intensity pattern in the products is equivalent to the EPR spectrum of the paramagnetic intermediates. Yet, the polarizations contain further, and much more specific, information. An EPR spectrum merely yields a set of coupling constants, but for nonequivalent protons present in the same number (e.g., eight protons with eight different coupling constants in the norbornene moiety of **III**) it is not possible to relate a particular hyperfine coupling constant to a particular proton without resorting to additional experiments. In contrast,<sup>60</sup> the CIDNP experiment assigns to each proton in the products its hyperfine coupling constant in the intermediate. Our identification of the intermediate **III** partly relied on this aspect of CIDNP as well, which is obviously of great diagnostic value. However, this peculiarity of CIDNP can also be regarded, and put to use, in a different manner, namely that in effect the protons are labeled with their hyperfine coupling constants. Since these labels are attached at the paramagnetic stage of the reaction but observed in the products, structural changes occurring on the route from the intermediates to the products can thus be monitored.

Given the structure of the biradical derived above it is clear that the pathway from it to the oxetane must involve a rearrangement of the hydrocarbon-based moiety. By utilizing the polarization patterns, it is possible to trace the positions of the protons during this rearrangement. This has already been done implicitly by our numbering of the protons in the norbornene parts of **I** and **II**, which was chosen such that the intensity patterns agree. From the distribution of the labels in the two products, it is immediately seen that the relative positions of all protons except H<sup>2</sup>, H<sup>3</sup>, and H<sup>5</sup> are left unchanged in the rearrangement of the norbornene moiety, the connectivity being CH<sup>2</sup>-CH<sup>5</sup>-CH<sup>3</sup> in the oxolane and CH<sup>2</sup>-CH<sup>3</sup>-CH<sup>5</sup> in the oxetane. Hence, it seems extremely unlikely that this exchange takes place by a series of hydrogen migrations. Rather, there must be a skeleton rearrangement of the three carbon atoms bearing these protons, namely a 1,2-shift of a vinyl group: C<sup>1</sup>=C<sup>2</sup>- is bonded to C<sup>5</sup> in **I**, and to C<sup>3</sup> in **II**. All other connectivities, except to the quinone moiety, are identical in **I** and **II**. As it is well known that migrations of vinyl groups

Chart 2



in free radicals occur via a cyclopropylmethyl intermediate,<sup>61</sup> the mechanism displayed in Chart 2 is consistent both with the structures of **I** and **II** and with their polarization patterns. This mechanism has already been inferred<sup>6,8</sup> from the structures of the reaction products; our CIDNP experiments furnish direct evidence for the vinyl 1,2-shift. By this rearrangement, the 1,5-biradical **III** is converted into a 1,4-biradical **IV**, which is an obvious precursor to **II**. The fact that formation of the oxetane in a triplet state is precluded by thermodynamics, as established in the previous section, shows that intersystem crossing must occur in **IV**.

AM1 calculations yield identical heats of formation for **III** and **IV** (within 1 kJ/mol of each other). This is not surprising since the structures of **III** and **IV** are very similar, and the change in the connectivity of the norbornene and quinone fragments is accompanied neither by steric nor by conjugative effects. While absolute values of  $\Delta H_f$  may not be meaningful owing to the overestimation of ring strain by AM1 (*cf.* ref 55), relative values should thus be quite reliable in this case. In contrast, significantly higher  $\Delta H_f$  is calculated for the nortricyclyl intermediate **V**, the difference being about 60 kJ/mol. However, after taking into account the errors in  $\Delta H_f$  of the parent compounds, this reduces to about 20 kJ/mol, which probably represents an upper limit still;<sup>62</sup> for the unsubstituted C<sub>7</sub>H<sub>9</sub><sup>\*</sup> radical, an energy difference between the nortricyclyl form and the norbornenyl form of 8...11 kJ/mol was obtained<sup>63</sup> experimentally, and EPR studies indicate<sup>50</sup> that oxygen substitution further stabilizes the nortricyclyl form. We are thus inclined to believe that the nortricyclyl biradical **V** possesses higher energy than the norbornenyl biradicals **III** and **IV**, the difference, however, being small.<sup>64</sup>

(61) (a) Montgomery, L. K.; Matt, J. W.; Webster, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 923-934. (b) Montgomery, L. K.; Matt, J. W. *J. Am. Chem. Soc.* **1967**, *89*, 934-941, 6556-6564.

(62) For norbornene and tricyclo[2.2.1.0<sup>2,6</sup>]heptane the differences between computed and experimental<sup>56</sup> values of  $\Delta H_f$  are 19 and 60 kJ/mol. Assuming these errors to be specific for the respective ring system,  $\Delta H_f$  of **V** must be reduced by 41 kJ/mol relative to  $\Delta H_f$  of **III**. Actually, the correction should presumably be even larger because of the additional strain<sup>55</sup> in the hydrocarbon skeleton that is introduced by the sp<sup>2</sup> radical center. It is interesting that in the case of the parent hydrocarbons the experiments show the tricyclic isomer to be preferred energetically, the differences between the heats of formation, however, being less than 8 kJ/mol.<sup>56</sup>

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(59) Beck, S. M.; Brus, L. E. *J. Am. Chem. Soc.* **1982**, *104*, 1103-1104.

(60) Roth, H. D. *Z. Phys. Chem. (Munich)* **1993**, *180*, 135-158.

Finally, from the CIDNP results it can be concluded that formation of **I** and **II** is not accompanied by biradical cleavage to give the quinone and norbornadiene or quadricyclane. As Charts 1 and 2 show, cleavage of **IV** and **V** would yield **N** and **Q**, respectively; since both biradicals result from the triplet channel of **III**, the bridge protons ( $H^7$  and  $H^{7'}$ ) would display strong absorption and one proton at the bridgehead ( $H^1$ ) strong emission. Cleavage of **III** should lead to another  $C_7H_8$  valence isomer that may possibly rearrange to give **N** or **Q**. In any case, two of the protons in the final product would be strongly polarized in emission and a third one in absorption. However, under conditions where all polarizations can be traced back to the biradical **III**, i.e. in the reactions with quadricyclane in a nonpolar solvent or with norbornadiene in any solvent, no polarizations of the educt nor of its valence isomer can be detected. Their absence unambiguously excludes such a biradical scission, which is in striking contrast to the photoreactions of quinones with anetholes, where scission of the singlet 1,4-biradical was found to be almost as efficient as ring closure.<sup>23</sup> This also shows that sensitized isomerization of the starting hydrocarbon by this "addition-elimination" pathway, as has been proposed in the literature,<sup>9</sup> does not occur for the systems investigated in this work.

**Absence of Polarizations from Biradicals IV and V.** The spectra (compare Figure 1, bottom trace) do not give any indication that CIDNP is generated in biradical **IV** as well. In this case,  $H^5$ ,  $H^6$ , and  $H^1$  would bear the largest polarizations, because the spin density distributions in **III** and **IV** should certainly be very similar; one would expect an intensity ratio of about 100:-85:16 for them, by analogy with the corresponding protons in **III** ( $H^7$ ,  $H^1$ , and  $H^6$ , in that order). As the initial multiplicity of **IV** must be triplet but the oxetane is formed from the singlet biradical **IV**,  $H^6$  should thus display absorption,  $H^5$  and  $H^1$  emission. While CIDNP from the triplet exit channel of **III** accidentally leads to the same phases of these protons, the intensity pattern observed for **II** (weak emission for II-5, weak absorption for II-6, and strong absorption for II-1, with a ratio of approximately 15:-19:100) is just the opposite to that predicted for CIDNP arising in **IV**. Hence, there can only be an insignificant contribution, if at all, of polarizations from the latter species.

With regard to CIDNP, the behavior of the structurally similar biradicals **III** and **IV** is thus totally divergent. We ascribe this effect to the distances between the radical centers, which are different for these two intermediates. As the evolution of S-T<sub>0</sub>-type nuclear spin polarizations requires a few nanoseconds for radical pairs,<sup>10</sup> and presumably much longer in the case of a biradical owing to the greater influence of the exchange interaction, the lifetime  $\tau$  of **III** must be larger than this, which is consistent with the observed increase of the CIDNP intensities on a time scale of the order of 100 ns. Conversely, the absence of CIDNP from **IV** puts  $\tau$  of the latter biradical well below this value. This could also explain the failure to detect a lag between formation of **I** and **II**. It is known<sup>41</sup> that intersystem crossing, which usually decides biradical lifetimes, proceeds most efficiently if the two orbitals bearing the unpaired electrons overlap but are orthogonal to each other. According to AM1, only minimal deviations from the equilibrium geometry of **IV** are necessary to realize such a situation, with the distance between the radical centers being about 3.1 Å. In contrast, for

**III** these calculations predict a geometry less favorable for intersystem crossing, demanding somewhat larger distortions that are accompanied by considerable interactions between protons  $H^8$  or  $H^9$  of the quinone part and protons  $H^1$  and  $H^6$  of the norbornene moiety (see Chart 1); even so, the distance between the radical centers in that conformation of **III** is greater by 0.6 Å than in the corresponding conformation of **IV**. On the one hand, this will cause a higher rate of intersystem crossing in **IV**, and thus a shorter lifetime. On the other hand, the mean exchange interaction in **IV** is therefore certainly larger than in **III**, which will decrease the rates of S-T<sub>0</sub> mixing. Both effects work in the same direction. Hence, the absence of polarizations from the 1,4-biradical **IV** does not seem unreasonable.

The nortricycyl intermediate **V** might also appear to be a potential source of CIDNP but the polarization patterns again rule this out: The corresponding radical is known<sup>50</sup> to have one large hyperfine coupling constant for the proton at the radical center ( $H^3$  according to our numbering), of almost the same magnitude as  $a_{H^1}$  in **IIIb**, and very small ones for the other protons, the values lying below 0.1 mT. As the signals of  $H^3$  in the products are among the weakest in the CIDNP spectra and must largely be attributed to polarizations arising in radical ion pairs, generation of CIDNP in **V** is thus negligible.

The lifetime of **V** may provide an explanation for the absence of nuclear spin polarizations from this biradical as well, in connection with another factor, namely that S-T<sub>0</sub>-type CIDNP cannot be observed in a reaction product if this is formed with identical yield from singlet and triplet intermediates. The structure of **V** shows that a combination of the two radical centers is impossible regardless of the electron spin multiplicity, since they are shielded from each other by the bridge. Thus, the only obvious intramolecular decay processes of **V** are rearrangements to give **III** or **IV**; intermolecular reactions with scavengers may also be possible if they take place at one radical moiety only. All conceivable chemical processes of this biradical therefore do not depend on the electron spin multiplicity, so the occurrence of an electron-spin selective reaction at a later stage would be a necessary condition for S-T<sub>0</sub>-type CIDNP. This is improbable for the direct decay pathway via **IV**: a rearrangement of **V** to give **IV** would chiefly lead to the oxetane **II** regardless of the initial multiplicity, because intersystem crossing of the Paterno-Büchi biradical **IV** is faster than the (endergonic) rearrangement back to **V**. Hence, even if opposite nuclear spin polarizations were created in the singlet and triplet states of **V**, they would largely cancel in **II**. In contrast, CIDNP generated in **V** would become detectable if this intermediate rearranged to **III**, since geminate recombination of the latter species is possible in the singlet state only. It is known that cyclopropylmethyl-homoallyl rearrangements are reversible,<sup>65</sup> and that cleavage of the ring preferentially takes place for the bond possessing the greater overlap with the orbital bearing the unpaired electron.<sup>66</sup> Molecular frameworks as well as AM1 calculations show that in our systems an almost perfectly bisected conformation of the cyclopropylmethyl radical is frozen, so scission of either bond is equally likely. Cleavage of bond "B" of the cyclopropane ring leads back to **III**, cleavage of bond "A" to **IV**. Once formed, **V** will therefore partition between **III** and **IV** in a ratio of approximately 1:1. Owing to the reversibility of the reaction, the lower stability of the nortricycyl system implies that the reaction **V** → **III** is faster than the reverse process, by a factor of 10 per 5.7 kJ/mol difference in  $\Delta G^\ddagger$ ; the partitioning of **V** introduces another factor of 2. Hence, we expect the mean life of **V** to be noticeably

(64) From the temperature dependence of the relative CIDNP signal intensities in **I** and **II**, an activation energy of 14 kJ/mol is obtained for the rearrangement **III** → **V** (Goez, M.; Frisch, I. Manuscript in preparation). Since no significant entropic changes are to be expected in this reaction, this value constitutes an upper limit for the free-enthalpy difference between the two biradicals.

(65) Efflo, A.; Griller, D.; Ingold, K. U.; Beckwith, A. L. J.; Serells, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1734-1737.

(66) Nonhebel, D. C. *Chem. Soc. Rev.* **1993**, 347-359.

lower than that of **III**, the lifetime of the nortricycyl intermediate not being limited by intersystem crossing, but by chemical decay to another biradical.

Although in retrospect a rationalization of the absence of S-T<sub>0</sub>-type CIDNP from **IV** and **V** thus seems to be possible, the strong effect of slight geometric changes, such as between **III** and **IV**, on the polarizations is striking. The crucial dependence of biradical CIDNP on small structural variations within a series of related molecules has already been pointed out by Doubleday.<sup>14a</sup> More detailed investigations of this phenomenon would appear desirable.

**S-T<sub>0</sub>-Type CIDNP from Biradical III.** The most common spin-sorting mechanism<sup>16</sup> underlying S-T<sub>0</sub>-type CIDNP is the competition of intersystem crossing with a process that is independent of the electron spin multiplicity, such as escape from the cage in the case of radical pairs, or reaction with a singlet scavenger<sup>39</sup> in the case of long-chain biradicals. For the 1,5-biradical **III**, the rearrangement to give the 1,4-biradical **IV** (Chart II) obviously provides such a spin-independent reaction because it solely involves one radical moiety. This "escape" route owes its feasibility to the fact that intersystem crossing of the resulting Paterno-Büchi biradical **IV** is fast, and this species therefore acts as a chemical sink. On the other hand, efficient spin sorting by the mechanism described is only possible because the rates of the two competing reactions of **III**, intersystem crossing and rearrangement, are comparable. Thus, a fairly special situation may be realized in the norbornadiene/quadricyclane systems. This might explain why there is no precedent for generation of S-T<sub>0</sub>-type CIDNP involving such a process, a skeleton rearrangement of a biradical.

Another means of achieving spin sorting in biradicals would be to furnish a reaction that takes place predominantly in the triplet state, in addition to geminate recombination, which is usually open to the singlet state only. To the best of our knowledge, this has also not been realized so far, but the oxygen-scavenging experiment may be an example for this. By the interplay of nuclear spin selective intersystem crossing with the two different termination processes possible for singlet and triplet biradicals, S-T<sub>0</sub>-type polarizations can be generated in the reaction products of **III**: Those nuclear spin states that favor intersystem crossing to the singlet state are overpopulated in the product of ring closure, the oxolane **I**, the others in the scavenging products. Still, this mechanism is not very efficient for two reasons. First, the life of **III** is shortened by the scavenger, so the extent of nuclear spin selective S-T<sub>0</sub> mixing is decreased.<sup>67</sup> Second, oxygen scavenging does not necessarily occur by a chemical reaction, i.e. formation of a combination product of the biradical with O<sub>2</sub>; rather, it can proceed by Heisenberg spin exchange to a considerable degree.<sup>68</sup> As the latter process provides a pathway for intersystem crossing that is independent of the nuclear spin states, it does not lead to polarizations. Hence, in the presence of oxygen CIDNP intensities from **III** should be but small in the oxolane **I**. However, no biradical polarizations can be transferred to the oxetane **II**, which is formed via the triplet exit channel of **III**, because the rearrangement of **III** to give **IV** is not fast enough

(67) A rate constant of  $6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  was measured for O<sub>2</sub> quenching of a Norrish II 1,4-biradical (Small, R. D.; Scalano, J. C. *J. Phys. Chem.* **1977**, *81*, 2126–2131). Assuming this value for scavenging of **III** by oxygen, and a saturation concentration of O<sub>2</sub> in acetonitrile of about 10<sup>-2</sup> M (Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1993), the life of the triplet biradical should thus be reduced to at least 20 ns. This appears to be short enough to interfere with CIDNP generation in these systems considering the time-resolved CIDNP experiments, which indicate a biradical lifetime of the order of 100 ns in the absence of oxygen.

(68) Caldwell, R. A.; Creed, D. J. *Phys. Chem.* **1978**, *82*, 2644–2652.

to compete with the scavenging reaction. Thus, the two main effects of oxygen on the biradical polarizations in our systems, weak biradical polarizations in **I** on the one hand, and no biradical polarizations in **II** on the other, are readily explained with the reaction mechanism of Chart 2, which is thus consistent with all the experimental results.

**Pathways of Biradical Formation.** The identical biradical polarizations in the reactions with norbornadiene and those with quadricyclane indicate identical decay pathways of **III** in both systems; the differences found (higher yield of **II**, lower yield of **III**, and absence of polarizations from radical ion pairs in the case of **N**) must be due to stages of the reaction that precede **III**.

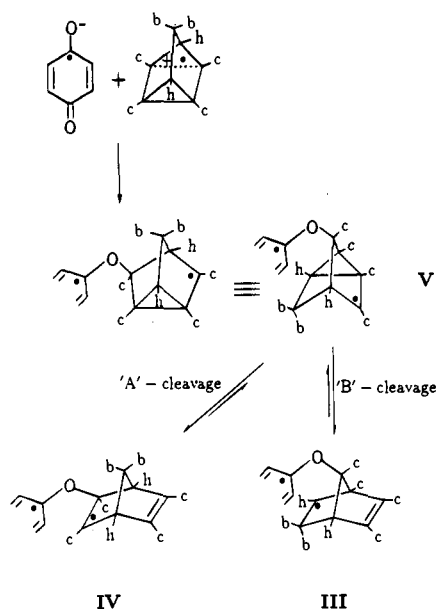
This implies that the polarizations from radical ion pairs, which are observed with **Q** only, arise at an earlier point of the reaction sequence than the biradical polarizations. In a recent CIDNP investigation<sup>23</sup> of the photoreactions of quinones with anetholes, we found that cycloadducts (i.e. oxetanes) are formed from correlated radical ion pairs in triplet states that undergo geminate recombination to give triplet biradicals, whereas radical ion pairs of singlet multiplicity decay by back electron transfer, regaining the educts. The superposition of "early" polarizations from the triplet exit channel of radical ion pairs Q<sup>+</sup>S<sup>-</sup> and "late" polarizations from biradicals of initial multiplicity triplet suggests that this mechanism applies to the systems quinone/quadricyclane too; the polarizations of the quinones **S** and of **Q** are also in accordance with it, as are the CIDNP signals of the product norbornadiene, which can be explained by that fraction of radical cations which escape geminate recombination and isomerize outside the cage. The fact that polarizations from radical ion pairs appear in the oxolane **I** as well, although a direct reaction of Q<sup>+</sup> and S<sup>-</sup> to give this compound is hardly conceivable, strongly supports this two-stage mechanism.

Further corroboration is obtained from the intensity patterns of the radical ion pair polarizations in **I** and **II**. These "CIDNP labels" again allow one to trace the structural changes occurring on the way from the intermediate in which the polarizations are generated, Q<sup>+</sup>S<sup>-</sup>, to the products. The radical cation of quadricyclane<sup>69</sup> possesses three different hyperfine coupling constants<sup>26</sup> only, which we denote with "c", "b", and "h" for the protons at the cyclobutane ring, the bridge, and the bridgeheads, respectively. The positions of these protons in the biradicals leading to the cycloadducts can be seen in Chart 3. Together with the results of the preceding section, these findings can be rationalized by geminate recombination of the triplet pairs <sup>3</sup>Q<sup>+</sup>S<sup>-</sup> to give the triplet biradical with the nortricycyl skeleton, <sup>3</sup>**V**. The combination must take place at an *exo* position of the radical cation because **I** and **II** are the only cycloaddition products in the quadricyclane systems. As the route to this particular biradical requires the smallest structural changes of the hydrocarbon moiety, it is very plausible; it is also consistent with the product distribution (see below). This entry point to the three interconverting biradical species was already postulated in earlier work,<sup>6,8</sup> although the mechanistic importance of radical ions does not seem to have been recognized.

The results of the experiments in the presence of O<sub>2</sub> also bear out the mechanism of Chart 3. Since oxygen completely suppresses the biradical polarizations in **II** by scavenging the 1,5-biradical **III** but does not affect the polarizations from Q<sup>+</sup>S<sup>-</sup> in **II** there must be a pathway from the radical ion pairs

(69) The formula for Q<sup>+</sup> given in Chart 3 is not intended to represent the geometry or the actual electron distribution of this species correctly, the latter being impossible within the limit of Lewis structures.

Chart 3



to the oxetane that does not touch **III**. This is provided by the cleavage of bond "B" (compare Chart 2) which leads from the nortricycyl intermediate **V** to the Paterno-Büchi biradical **IV**. Neither species can be intercepted efficiently by a chemical reaction with the triplet scavenger, the first because the two radical centers are shielded and the second for lifetime reasons. On the other hand, Heisenberg spin exchange between  $O_2$  and **IV** or **V** would not affect the polarizations from the radical ion pairs, because at the biradical stage their generation is already finished, and they are simply transferred to the products.

The obvious question is whether the pathway via radical ion pairs is the only pathway to **V**, or if a direct reaction of  $^3S + Q$  to give **V** occurs as well. A conclusive answer would be possible if the radical ion pair  $Q^{+\bullet}S^{\bullet-}$  could be prepared without the intermediacy of the triplet quinone. In principle, electron-transfer sensitization<sup>70</sup> should be a feasible means to achieve this. With this technique, an auxiliary sensitizer **A** is used to generate a primary radical ion pair  $Q^{+\bullet}A^{\bullet-}$ , which is then scavenged by **S** during diffusive excursions to give the desired pair  $Q^{+\bullet}S^{\bullet-}$ . If the excitation wavelength can be chosen such that the light is not absorbed by **S**, and if the relative positions of the energy levels of **S** and **A** preclude energy transfer,  $^3S$  is bypassed<sup>71</sup> while the same radical pair is obtained as upon direct excitation of **S**. For the photocycloadditions of quinones with anetholes, we could establish<sup>23</sup> in this way that formation of biradicals from radical ion pairs is the main mechanistic route to the products. Unfortunately, our attempts to apply this method to the systems investigated in this work have been unsuccessful as yet.

However, the observed variations with the sensitizer of the amounts of polarization from radical ion pairs and biradicals strongly suggest that biradical formation according to Chart 3 constitutes the predominant pathway in the photoreactions with quadricyclane, the reasoning being as follows. In addition to

(70) (a) Mattes, S. L.; Farid, S. *Org. Photochem.* **1983**, *6*, 233–326. (b) Chanon, M.; Ebersson, L. In *Photoinduced Electron Transfer. Part A. Conceptual Basis*; Fox, M. A., Chanon, M., Eds.; Elsevier: New York, 1988; pp 409–597. (c) Mattay, J. *Synthesis* **1989**, 233–252 and references therein.

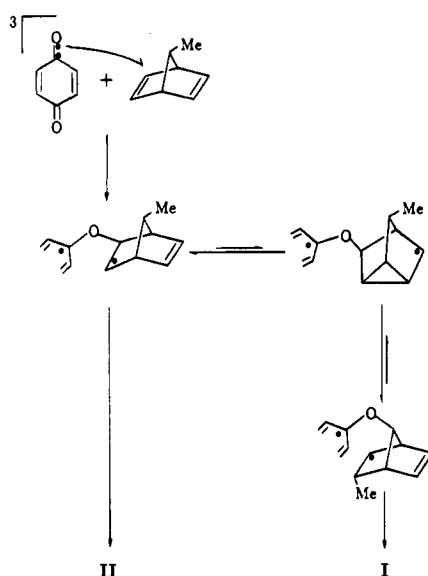
(71) A necessary condition for this is that  $^3S$  not be formed by back electron transfer of  $Q^{+\bullet}S^{\bullet-}$ . This is fulfilled in our case because electron return of triplet pairs is not feasible energetically for those systems that form cycloadducts.

escape from the cage, geminate recombination of  $Q^{+\bullet}S^{\bullet-}$  to give  $^3V$  provides another exit channel for the triplet pairs. Efficient formation of  $^3V$  therefore leads to a low escape probability on the one hand, and to some extent interferes with CIDNP generation by shortening the lifetime of the radical ion pairs on the other. Thirdly, the yield of  $^3V$  becomes high. With regard to the norbornadiene polarizations the first two effects are cumulative because **N** is the product<sup>2</sup> of escaping radical cations  $Q^{+\bullet}$ , and these CIDNP signals are therefore decreased substantially. As far as the radical ion pair polarizations in the products are concerned these two effects oppose each other, the higher probability for transfer of CIDNP from  $Q^{+\bullet}S^{\bullet-}$  to  $^3V$  being overcompensated by a lower degree of nuclear spin polarization attained in the radical ion pairs, so these superimposed polarizations are somewhat reduced, though not as strongly as in **N**. The third effect finally increases the biradical polarizations in the products. Conversely, less efficient formation of  $^3V$  causes an intense norbornadiene signal but still noticeable polarizations from radical ion pairs in the cycloadducts, while the biradical polarizations are decreased considerably. All this is in accordance with the experimental results, the systems **B/Q** and duroquinone/**Q** being typical examples for these two cases (compare Figure 1, bottom and center traces). In contrast, a predominance of the direct reaction of  $^3S$  with **Q** to give **V** seems to accommodate the experimental facts less well. While this process would imply an inverse relationship between the yields of biradicals and radical ion pairs, and could thus account for the changes of the ratio of the biradical polarizations to the total of the radical ion pair polarizations just as well, it should hardly affect the partitioning of the polarizations from  $Q^{+\bullet}S^{\bullet-}$  between the cycloadducts and **N**; besides, the signal of regenerated **Q** should be low when the efficiency or biradical formation is high and *vice versa*, which is contradicted by the experiments (see Figure 1). Hence, we conclude that formation of **V** by geminate recombination of  $Q^{+\bullet}S^{\bullet-}$  prevails over a possible direct reaction without initial charge separation. The results in  $CDCl_3$  do not countermand this as the lack of CIDNP from radical ion pairs in this nonpolar solvent does not imply that such pairs do not exist, but only that their Coulomb interactions suppress  $S-T_0$  mixing.<sup>37</sup>

The absence of radical ion pair polarizations in the corresponding reactions with norbornadiene must mean that in these cases the biradical is formed without the intermediacy of pairs  $N^{+\bullet}S^{\bullet-}$ . An explanation by unfavorable magnetic parameters of the radical pairs is untenable, since the largest hyperfine coupling constants of  $Q^{+\bullet}$  and  $N^{+\bullet}$  are very similar<sup>26,29</sup> and the *g*-values of these species should be nearly identical; besides, with sensitizers such as chloranil, where no cycloaddition takes place, **N** and **Q** exhibit comparable polarizations from radical ion pairs in the regenerated starting materials.

Instead of nuclear spins, i.e. CIDNP labels, chemical labels must be used in this case to trace the formation route of the biradical. The  $CH_3$  group of 7-methylnorbornadiene serves as such a chemical label. As Chart 4 shows, the stereospecific incorporation of this substituent into the 7-position of **I** and **II** is consistent with the same general reaction scheme as above, the coupling with the benzoquinone moiety again occurring in an *exo* position, and furthermore at the opposite side of the bridge as that taken by the methyl group. As reported before,<sup>6,8</sup> the initially formed biradical is not **V** but **IV** in this case, which is plausible from the structural similarity with the educt, and which also provides a natural explanation for the much higher

Chart 4



relative yield of **II** as well as the lower CIDNP intensities in the photoreactions with **N** than those with **Q**.

Formation of **V** or **IV** as primary biradical intermediates in the reactions of **Q** or **N** (Charts 3 and 4) is in agreement with our experimental observation that *two* cyclopropane rings or homoconjugated double bonds are prerequisites for these cycloadditions. It is interesting that **III**, which constitutes the only source of biradical polarizations in our systems, is a *secondary* species in the reactions of both quenchers. We emphasize that the structural changes from the educts to **III** can nevertheless be monitored as well, by an additional labeling process performed at an earlier stage of the reaction: With **Q**, CIDNP labels are employed that are affixed at the stage of the radical ion pairs; with **N**, a chemical label is used that is already present in the educts.

It has been proposed<sup>8</sup> that photocycloadditions of other carbonyl compounds to norbornadiene proceed by a mechanism that involves sensitized isomerization of **N** to **Q** as a first step, followed by addition of the carbonyl triplet to the resulting quadricyclane. The different behavior of **N** and **Q** with regard to CIDNP rules out such a mechanism for our systems: isomerization of **N** before biradical formation would lead to the same superposition of radical ion pair CIDNP and biradical CIDNP as found in the reaction with **Q**. Since isomerization of **N** via its triplet state would not be feasible with our quinones because their triplet energies are much too low, it might be argued that our mechanistic conclusions do not apply to the systems studied in ref 8. However, our CIDNP results demonstrate that *there exists a pathway without preceding isomerization* for biradical formation from our triplet sensitizers and norbornadiene.

#### Interpretation of Sensitizer and Quencher Dependence.

The different routes to the biradicals in the photocycloadditions with quadricyclane and with norbornadiene, via intermediate radical ion pairs in the former case and direct in the latter, can be rationalized with the free enthalpy  $\Delta G^{\circ}_{ET}$  for electron transfer quenching of the sensitizer triplet. Redox potentials and triplet energies of sensitizers and quenchers have been compiled in Table 1. It is seen that electron transfer from the hydrocarbon to the excited quinone is more endergonic by 60 kJ/mol with norbornadiene than in the case of quadricyclane. With the data of Table 1,  $\Delta G^{\circ}_{ET}$  is calculated to be  $-20$  kJ/mol for quenching of **3B** by **N**. The driving force for formation of radical ion pairs is thus not very large in this system; in view of a possible

Table 1<sup>a</sup>

compound	$\Phi$ [V vs SCE]	$E_T$ [kJ mol <sup>-1</sup> ]
quadricyclane <b>Q</b>	+0.91 <sup>b</sup>	222...242 <sup>c</sup>
norbornadiene <b>N</b>	+1.54 <sup>b</sup>	257 <sup>d</sup>
1,4-benzoquinone <b>B</b>	-0.52 <sup>e</sup>	220 <sup>f</sup>
2,6-dimethyl-1,4-benzoquinone	-0.61 <sup>g</sup>	220 <sup>h</sup>
1,4-naphthoquinone	-0.71 <sup>e</sup>	225 <sup>i</sup>
menadione	-0.80 <sup>e</sup>	225 <sup>j</sup>
duroquinone	-0.84 <sup>k</sup>	218 <sup>l</sup>
2,3-dichloro-1,4-naphthoquinone	-0.45 <sup>e</sup>	245 <sup>i</sup>
9,10-anthraquinone	-0.95 <sup>e</sup>	261 <sup>l</sup>
chloranil	-0.01 <sup>m</sup>	261 <sup>m</sup>
2,3-dichloro-5,6-dicyano-1,4-benzoquinone	+0.52 <sup>e</sup>	268 <sup>l</sup>
xanthone	-1.76 <sup>n</sup>	310 <sup>o</sup>
benzophenone	-1.83 <sup>n</sup>	287 <sup>p</sup>

<sup>a</sup> The table displays the potentials  $\Phi$  in acetonitrile for the oxidation of the quenchers **Q** and **N** and for the reduction of the sensitizers, and the triplet energies  $E_T$  of these compounds. <sup>b</sup> Reference 2. <sup>c</sup> Reference 1. <sup>d</sup> Helms, A. M.; Caldwell, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 358–361. <sup>e</sup> Sasaki, K.; Kashimura, T.; Ohura, M.; Ohsaki, Y.; Ohta, N. *J. Electrochem. Soc.* **1990**, *137*, 2437–2443. <sup>f</sup> Reference 59. <sup>g</sup> Driebergen, R. J.; Moret, E. E.; Janssen, L. H. M.; Blauw, J. S.; Holthuis, J. J. M.; Postma Kelder, S. J.; Verboom, W.; Reinhoudt, D. N.; van der Linden, W. E. *Anal. Chim. Acta* **1992**, *257*, 257–273. <sup>h</sup> Herre, W.; Weis, P. *Spectrochim. Acta, Part A* **1973**, *29*, 203–205. <sup>i</sup> El'tsov, A. V.; Studzinskii, O. P.; Grebenkina, V. M. *Russ. Chem. Rev.* **1977**, *46*, 185–227. <sup>k</sup> Peover, M. E. *J. Chem. Soc.* **1962**, 4540–4549. <sup>l</sup> This work; determined from the shoulders at maximum wavelength in the phosphorescence spectra, which were recorded in EPA at 77 K with a Perkin-Elmer MPF-44 photometer equipped with an Aminco Phosphoroscope C26. <sup>m</sup> Kasha, M. *Chem. Rev.* **1947**, *41*, 401–419. <sup>n</sup> Given, P. H.; Peover, M. E.; Schoen, J. *J. Chem. Soc.* **1958**, 2674–2679. <sup>o</sup> Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747–7753. <sup>p</sup> Saltiel, J.; Curtis, H. C.; Metts, L.; Miley, J. W.; Winterle, J.; Wrighton, M. J. *Am. Chem. Soc.* **1970**, *92*, 410–411.

uncertainty of the parameters, it seems even conceivable that the reaction is not exergonic at all. For the other sensitizers that were found to give cycloadducts with **N**, still less negative values are computed for  $\Delta G^{\circ}_{ET}$ . Hence, it appears very likely that formation of radical ion pairs is not efficient in the reactions of these quinones with norbornadiene because this process is not, or not sufficiently, exergonic; electron transfer quenching by **N** can only be achieved with the two sensitizers chloranil and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, for which  $\Delta G^{\circ}_{ET}$  is indeed calculated to be strongly negative (but which do not lead to cycloadducts, as will be discussed below). With quadricyclane, on the other hand, where photoinduced electron transfer is certainly exergonic with all quinones employed, our sensitizers without exception yield radical ion pairs preceding the biradicals. The preference of the indirect pathway to biradicals via electron transfer quenching, whenever this process is feasible, over their direct formation may be ascribed to two factors. First, the geometric changes occur more gradually with the former route, so less activation energy is needed for each step. Second, the distance dependence of these two processes is different: an electron can be transferred over 7 Å and more<sup>72</sup> while formation of a biradical requires the reactants to be in direct contact.

For the system **B/Q**, we estimate the driving force of biradical formation from radical ion pairs, i.e. of the process  $Q^{+}B^{-} \rightarrow V$ , as follows.  $\Delta H_f$  for biradical **IV** is calculated from the value for the oxetane **II** by subtracting the contributions for strain of the four-membered ring and for one *syn* interaction (see above) and by replacing the groups C–(H)(C)<sub>3</sub> and C–(C<sub>d</sub>)<sub>2</sub>–(C)(O) by C\*–(H)(C)<sub>2</sub> and C\*–(C<sub>d</sub>)<sub>2</sub>(O), respectively. The increment for the former radical group is +172.3 kJ/mol.<sup>74</sup> For

the latter group, we compare 1,4-benzoquinone with its neutral semiquinone radical. As was shown<sup>73</sup> by a thermodynamic cycle,  $\Delta H_f$  of the latter species is more negative by 30 kJ/mol than  $\Delta H_f$  of the parent compound. In the transformation from the quinone to its neutral radical, two groups of  $C_d-(H)(CO)$  (+20.9 kJ/mol each)<sup>57</sup> are converted into  $2 \times C_d-(H)(C^*)$ , to which we assign the average of  $C_d-(H)(C)$  (+35.9 kJ/mol)<sup>57</sup> and  $C_d-(H)(C_d)$  (+28.4 kJ/mol).<sup>57</sup> In addition,  $CO-(C_d)_2$  (-103.3 kJ/mol, see above) changes into  $O-(H)(C^*)$  plus  $C^*-(C_d)_2(O)$ . We take the increment for  $O-(H)(C^*)$  to be -158.6 kJ/mol since both  $O-(H)(C)$  and  $O-(H)(C_d)$  possess this value.<sup>57</sup> The group increment for  $C^*-(C_d)_2(O)$  should thus be +2.8 kJ/mol only. Hence, for  $\Delta H_f$  of the 1,4-biradical **IV** we get +192 kJ/mol. The reported<sup>74</sup> success of such a calculational procedure even for olefin triplets, which were regarded as 1,2-biradicals in that study, shows that effects of the exchange interaction should already be contained in the group increments. We assume that  $\Delta S^\circ$  for the reaction **IV**  $\rightarrow$  **II** is chiefly determined by the entropy contribution due to the oxetane ring in **II** (+115.9 J K<sup>-1</sup> mol<sup>-1</sup>).<sup>57</sup> At room temperature, the free enthalpy of **IV** is thus more positive by 90 kJ/mol than the value for the educts **B** + **N** in their ground states. As already mentioned,<sup>64</sup>  $\Delta H^\circ$  of the reaction **IV**  $\rightarrow$  **V** must be lower than +14 kJ/mol; furthermore, the entropy change during this reaction should be very small. Taking into account the differences in  $\Delta H_f$  for **N** and **Q** (see ref 55) and the redox potentials, we finally arrive at a value of -127 kJ/mol for  $\Delta G^\circ$  of the reaction  $Q^{+}S^{-} \rightarrow V$ . This process is thus strongly exergonic.

However, with regard to biradical formation steric effects seem to prevail over electronic effects. This is seen most clearly with the sensitizers 1,4-benzoquinone and 9,10-anthraquinone in the reaction with **Q**. From the redox potentials of these two compounds it is evident that the free enthalpy of the pair  $Q^{+}S^{-}$  relative to the respective starting materials is higher by 41 kJ/mol in the case of 9,10-anthraquinone. To estimate the electronic effects in the biradicals, we compare the differences between  $\Delta H_f$  for the neutral semiquinone radical and the ground state quinone in these two instances because the entropy changes should be identical in both systems. This difference is larger by 45 kJ/mol with 9,10-anthraquinone.<sup>73</sup> Hence, other things being equal, the driving force of the reaction  $Q^{+}S^{-} \rightarrow V$  should be almost the same with these sensitizers, so one would expect biradical formation to be highly exergonic also with 9,10-anthraquinone. Yet, these two sensitizers represent two extreme situations: with 1,4-benzoquinone, both **I** and **II** are formed in good yields, and large CIDNP signals are observed, which chiefly stem from the biradical **III**; with 9,10-anthraquinone, the oxetane **II** predominates, the overall yield is low, biradical polarizations are absent, and weak polarizations from radical ion pairs are detected in **II**.

The shift in the relative yields of the products is explained by the influence of the bulky substituents at the quinone fragment in the latter case. Molecular frameworks show that these effectively bar ring closure of the 1,5-biradical **III** while the steric demands are less strict with the 1,4-biradical **IV**. The polarizations from the radical ion pairs  $Q^{+}S^{-}$  are therefore mainly transferred to **II**. As the only decay channel left for **III** must be isomerization to **V**, which is independent of the electron spin multiplicity, S-T<sub>0</sub>-type CIDNP cannot arise in **III** any more. The reduced overall yield of products is finally rational-

ized with an increase of the energy of the biradicals due to strain and a higher activation barrier of biradical formation from  $Q^{+}S^{-}$ . The importance of these steric effects is corroborated by the results with the other sensitizers, which show a systematic trend toward lower product yields, predominance of **II** over **I**, and decrease of the biradical polarizations with increasing degree of substitution of the benzoquinone skeleton. The behavior of chloranil and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone can also be explained in the same manner. In this case, however, the energy of the radical ion pairs is so low that biradical formation is totally inhibited, and back electron transfer is the only deactivation channel remaining for  $Q^{+}S^{-}$  as well as  $N^{+}S^{+}$ .

Finally, these considerations provide a reason for the absence of CIDNP, both from radical ion pairs and from biradicals, in the reactions of **N** and **Q** with the sensitizers xanthone and benzophenone. With **N**, electron transfer quenching would be endergonic, so radical ion pairs cannot be formed at all. While this process is thermodynamically feasible for **Q**, the energy of the radical ion pairs  $Q^{+}S^{-}$  lies above the energy of  ${}^3Q + S$ . Hence, the radical ion pairs are probably bypassed by triplet-triplet energy transfer from  ${}^3S$  to **Q**, but even if they are formed, spin sorting could not occur because back electron transfer would be equally possible for singlet and triplet pairs. As the carbonyl group in both sensitizers is flanked by bulky phenyl substituents, polarizations cannot arise at the biradical stage either, as was the case with 9,10-anthraquinone, which possesses an obvious structural similarity to these two compounds.

## Conclusions

Three main conclusions emerge from this study.

Concerning the mechanism of the photocycloadditions of quinones with norbornadiene and quadricyclane, the most important aspect certainly is that one of the key intermediates has been observed for the first time by a spectroscopic method: 1,5-Biradicals **III** possessing a norbornenyl structural fragment have been identified unambiguously by the CIDNP intensity patterns in the products, which are characteristic signatures of their spin density distributions. To our minds, of almost equal significance is that the interconversions **III**  $\rightleftharpoons$  **IV** of 1,5-biradicals and 1,4-biradicals, the latter also having a norbornenyl skeleton, could be traced by "CIDNP-labeling", i.e. the use, as labels, of polarized nuclear spins that have a characteristic CIDNP intensity associated with a specific nucleus. Since these labels are attached at the stage of the paramagnetic intermediates, CIDNP labeling of the biradicals could be combined with a second labeling step, either by chemical labeling of the educts (in the case of norbornadiene) or by CIDNP labeling of a preceding intermediate (the radical ion pairs in the reactions with quadricyclane). In this way, it was possible to trace the pathways of both decay and formation of the biradicals.

Second, fairly unusual CIDNP effects were observed in this study. The polarizations are of the radical-pair type, i.e. CIDNP is generated by S-T<sub>0</sub> mixing, but they originate in the 1,5-biradical **III**. There are but very few reports<sup>13-16</sup> of S-T<sub>0</sub>-type CIDNP stemming from such a short-chain biradical. While the spin-sorting mechanism operating in **III** can be understood on the basis of known<sup>16</sup> principles, it is nevertheless unique: An "escape" pathway is provided by the (reversible) skeleton rearrangement of **III** to give the 1,4-biradical **IV** that possesses a higher intersystem crossing rate and therefore functions as a chemical sink. We are not aware of any precedent for such a mechanism of CIDNP generation. As the results of the present

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paper corroborate, the efficiency of spin sorting in biradicals is strongly influenced by small changes of the molecular geometry.<sup>14a</sup> Further investigations focussing on the dependence of biradical CIDNP on molecular structure therefore seem appropriate.

Third, in our opinion this work nicely demonstrates the power of photo-CIDNP spectroscopy in studies of complex reactions, and shows that this spectroscopic method combines the advantages of more than one experimental technique. On the one hand, both the analytical potential of EPR spectroscopy and that of high-resolution NMR spectroscopy are accessible to it, the latter direct and the former indirect, through the polarization patterns. On the other hand, it is sensitive to processes occurring on a nanosecond time scale, and in kinetic measurements it reaches the time resolution of conventional flash photolysis. It yields specific information about the multiplicities of the reacting species, information that is often different or impossible to obtain by other methods. And finally, it allows one to trace the pathways from the intermediates to the products in a similar way as labeling experiments do, because the polarizations are generated at an earlier stage than they are detected. As the results of the present study show, a fairly complete picture of a chemical reaction can be obtained in this way.

## Experimental Section

**Chemical Substances and Sample Preparation.** All sensitizers were purified by repeated sublimation at  $10^{-6}$  bar. Quenchers were doubly distilled under nitrogen at reduced pressure. 7-Methylnorbornadiene was prepared<sup>75</sup> by a Grignard reaction of 7-chloronorbornadiene, which was synthesized<sup>76</sup> via the 7-*tert*-butoxy derivative.<sup>77</sup> Deuterated solvents (ICB, 99.5% D) were dried over molecular sieves prior to use. If not stated otherwise, the quinone concentration in the samples was  $8 \times 10^{-3}$  M corresponding to an absorbance at the excitation wavelength of approximately 2; quencher concentrations of about  $1 \times 10^{-2}$  M were used. Samples were prepared in a dry atmosphere, deoxygenated by bubbling purified nitrogen through the solutions, and then immediately sealed.

**NMR Measurements.** Most <sup>1</sup>H-NMR spectra were recorded on a Bruker WM-250 spectrometer. For two-dimensional experiments and <sup>13</sup>C-NMR measurements a Bruker AM-400 spectrometer was used. All measurements were carried out in CD<sub>3</sub>CN at room temperature. Further

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details concerning product identification are given as supporting information. The NMR parameters of the photocycloadducts are also listed there.

**CIDNP Measurements.** These measurements were performed with a Bruker WM-250 spectrometer. The time base of all experiments was provided by a home-made programmable pulse generator. Both apparatus were controlled by an 80486-based multitasking workstation equipped with a Keithley AD-converter for data acquisition.

An excimer laser that was triggered by the pulse generator served as the light source. Side-on illumination of the samples was possible by a quartz rod and prism inserted into the probe. A detailed description of the optical setup can be found elsewhere.<sup>78,79</sup> An energy of 1...2 mJ per flash was absorbed in the samples as determined actinometrically.

The pulse sequences used for time-resolved<sup>80</sup> and pseudo-steady-state CIDNP measurements<sup>81</sup> have been described previously. Spectra obtained by these techniques are practically free from the effects of nuclear spin–lattice relaxation in the products. Moreover, unchanging background signals are suppressed by two orders of magnitude at least.

**Calculations.** MO calculations with the AM1 Hamiltonian<sup>82</sup> were carried out on an IBM 3090 computer with the program MOPAC 5.0. Energies of radicals and biradicals were calculated with the options “rhf” and “triplet biradical”, respectively.

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**Supporting Information Available:** Product structure evidence, <sup>1</sup>H- and <sup>13</sup>C-NMR parameters of the photoproducts in the system B/Q; <sup>1</sup>H-NMR parameters of the photoproducts in the other system (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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