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# Photoinduced Electron-Transfer Reactions of Aryl Olefins. 1. Investigation of the Paterno–Büchi Reaction between Quinones and Anetholes in Polar Solvents

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**Abstract:** The [2+2] photocycloadditions of quinones to *cis*- and *trans*-anethole in acetonitrile were studied by measurements of chemically induced dynamic nuclear polarization (CIDNP) and NMR analysis of the products. These reactions proceed with excellent regioselectivity to oxetanes; formation of cyclobutanes was not observed. With benzoquinone, anthraquinone, and naphthoquinone at room temperature, the predominant product is the thermodynamically most stable stereoisomer possessing *trans* configuration of the anethole moiety regardless of the configuration of the starting olefin. In the case of naphthoquinone, at low temperature good yields of additional stereoisomers are obtained in which the configuration of the educt anethole is preserved. Cycloaddition is accompanied by considerable one-way *cis*–*trans* isomerization of the olefin. The results of stationary and time-resolved CIDNP experiments showed that the polarizations of the photoproducts originate from a pathway that leads from correlated radical ion pairs of triplet multiplicity to triplet biradicals, whereas the educts are regenerated by back electron transfer of singlet pairs. By combining CIDNP detection with photoinduced electron-transfer sensitization, it was established that the pathway that gives rise to nuclear spin polarizations is also the main route to the products; a significant contribution of a direct reaction of exciplexes to biradicals is thus ruled out for the systems investigated. The product distribution and its temperature dependence is explained by conformational changes of the triplet biradicals. The biradicals are formed in conformations that are determined by Coulombic interactions between their precursors or in the transition state. Subsequent relaxation to an energetically more favorable conformation by thermally activated rotations around single bonds competes with intersystem crossing. The initial conformations finally lead to the low-temperature photoproducts, and the relaxed conformation leads to the high-temperature oxetane as well as (by scission of the singlet biradical) to *trans*-anethole, i.e., to one-way isomerization. The CIDNP measurements gave an activation energy for bond rotation of 11.5 kJ/mol and lifetimes of the initial triplet biradicals of 95 and 125 ps, which are very short but consistent with the failure of experiments to trap the biradicals with oxygen. For the singlet biradical in the relaxed conformation, the ratio of ring closure to scission was found to be 1.6 at 233 K and 1.0 at 330 K.

Photoinduced [2+2] cycloaddition of carbonyl compounds with alkenes to give oxetanes (the Paterno–Büchi reaction) has become of considerable synthetic importance[1] since its discovery[2] many years ago. Early investigations of this reaction led to the conclusion that bond formation proceeds stepwise, via a triplet biradical.[3] This was later confirmed by detection of this intermediate by picosecond absorption spectroscopy[4–6] as well as by scavenging experiments.[7] Charge-transfer interactions prior to biradical formation have been invoked to explain observations such as a dependence of the reaction rate on the ionization potential of the alkene[8–10] or exceptions[1a,9,11,12] from the "most stable biradical" rule.[2b,13] However, the extent of these interactions (intermediacy of an exciplex[1a,7a,9,14–16] or actual charge separation to give radical ion pairs[4,6,10,17–20]) is still subject to research. In those few cases where radical ions

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were detected by spectroscopic techniques in Paterno–Büchi reactions, widely differing conclusions were drawn with respect to their mechanistic role. They were taken to be mere byproducts resulting from irreversible heterolysis of triplet biradicals[4] or from reversible heterolysis of biradicals of both multiplicity,[6] and it was inferred that no charge transfer takes place prior to biradical formation.[6] In another investigation,[19] it was concluded that the biradicals are formed by encounters of free radicals, which have lost their spin correlation. One group considered[17] parallel reactions of exciplexes and contact ion pairs to give biradicals, and later[10] regarded radical ion pairs as precursors to zwitterions leading to the products, which would imply a singlet multiplicity of the pairs. Finally, singlet radical ion pairs were also assumed to be immediate precursors to the oxetanes.[20]

A convenient means to study reactions occurring via radical ion pairs and distinguish them from reactions involving exciplexes and short-chain biradicals only is provided by measurements of chemically induced dynamic nuclear polarization[21] (CIDNP). This phenomenon results from nuclear spin selective intersystem crossing that is induced by the interplay of electron Zeeman and hyperfine interactions during diffusive separations of intermediate radical pairs.[22] By this process, opposite nuclear spin polarizations are created in the singlet and triplet manifold of the pairs upon reencounter. If singlet and triplet pairs react to different diamagnetic products, these polarizations become observable and manifest themselves by anomalous line intensities (enhanced absorption or emission) in NMR spectra recorded during the reaction. The fairly rigid geometry of an exciplex excludes such a mechanism,[23] and generation of polarizations in a 1,4-biradical is also extremely unlikely.[19]

In addition to this, CIDNP is an attractive technique for the study of complex reaction mechanisms, because it yields information about precursors, intermediates, and products at the same time. The reaction products are observed by high resolution NMR spectroscopy; hence the method is often much more specific than, for instance, flash photolysis with UV/vis detection. The radicals involved can be identified, since the spin density distribution in the paramagnetic intermediates is reflected by the relative polarization intensities of the different protons.[23,24] Reactions of radicals within the cage may be distinguished from reactions of free radicals by time-resolved CIDNP experiments.[25] Finally, the electron spin multiplicity of the precursor and of the radical pair leading to a particular product may be obtained, because the polarization phases depend on both.

To our knowledge, there have only been two CIDNP investigations of Paterno–Büchi reactions so far.[19,20] In this work, we apply CIDNP techniques to the study of photocycloadditions of quinones to *cis-* and *trans*-anethole to give spirooxetanes. Similar systems have recently been investigated by other methods,[26] the interest in the photoadducts being stimulated by their possible use as anticancer agents.[26b] We present evidence that with our compounds full charge transfer takes place and correlated radical ion pairs in a triplet state are precursors to the biradicals.

**Table 1.** Sensitizers and Quenchers Used in This Work[a]

| compound | $E_S$ | $E_T$ | $\Phi_{red}$ | $E_{RIP}$ |
|---|---|---|---|---|
| *cis*-anethole (*c*-**A**) | ≳ 340[b] | 289[c] | +1.47[c] | – |
| *trans*-anethole (*t*-**A**) | >380[b] | 241[d] | +1.39[c] | – |
| 1,4-benzoquinone (**BQ**) | 247[e] | 210[e] | −0.51[f] | 191 |
| 1,4-naphthoquinone (**NQ**) | 263[e] | 224[e] | −0.71[f] | 210 |
| 9,10-anthraquinone (**AQ**) | 283[e] | 253[e] | −0.94[f] | 233 |
| 9-cyanoanthracene (**CNA**) | 299[g] | 164[g] | −1.46[h] | 283 |

[a] The table displays the name and abbreviation of the respeetive compound; energies $E_S$ and $E_T$ of its lowest excited singlet and triplet state (in kJ/mol); redox potentials in acetonitrile (reduction potentials in V versus SCE), positive values being valid for the couples ($X^{•+}/X$), negative values for ($X/X^{•-}$); and calculated (see footnote 29) energies, in kJ/mol, of the radical ion pair consisting of the radical anion of the respective compound with the radical cation of *c*-**A**, the corresponding values with the radical cation of *t*-**A** being lower by 8 kJ/mol. [b] Estimated from the onset of the UV absorption. [c] Reference 49. [d] Reference 62. [e] El'tsov, A. V.; Studzinskii, O. P.; Grebenkina, V. M. *Russ. Chem. Rev.* **1977**, *46*, 93–114. [f] Peover, M. E. *J. Chem. Soc.* **1962**, 4540–4549. [g] van der Donckt, E.; Barthels, M. R.; Delestine, A. J. *J. Photochem.* **1973**, *1*, 429–432. [h] Spada, L. T.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 391–393; Lewis, F. D.; Bedell, A. M.; Dykstra, R. E.; Elbert, J. E.; Gould, I. R.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 8055–8064.

## Results

**Choice of Reaction Systems.** The sensitizers and quenchers investigated, their abbreviations used in this work, and their relevant thermodynamical properties have been compiled in Table 1. The reactants were chosen to ensure a uniform pathway for photochemical desactivation, via electron transfer, and thus reduce the complexity of the reaction scheme as far as possible.

The following requirements are met in the quinone–anethole systems. At the excitation wavelength, the light is absorbed exclusively by the sensitizers. No evidence for formation of ground-state complexes could be detected in the UV/vis and NMR spectra of mixtures of the compounds. Energy transfer from singlet quinone to singlet anethole is not feasible thermodynamically. Intersystem crossing of the quinones **Q** to their triplet states ($\phi_{isc} \approx 1$)[27] is very rapid.[28] Hence, $^1$**Q** cannot be quenched to an appreciable degree with the anethole concentrations used in our experiments, even at a diffusion-controlled rate.

The energies of the radical ion pairs were calculated from the redox potentials[29] and are given in the table. Comparison with the triplet energy of the respective quinone shows that electron-transfer quenching of $^3$**Q** by the anetholes **A** is fairly exergonic, so it is expected to proceed diffusion controlled. Owing to the long life of $^3$**Q** (several microseconds),[30,31] quenching quantum yields in excess of 90% can be realized

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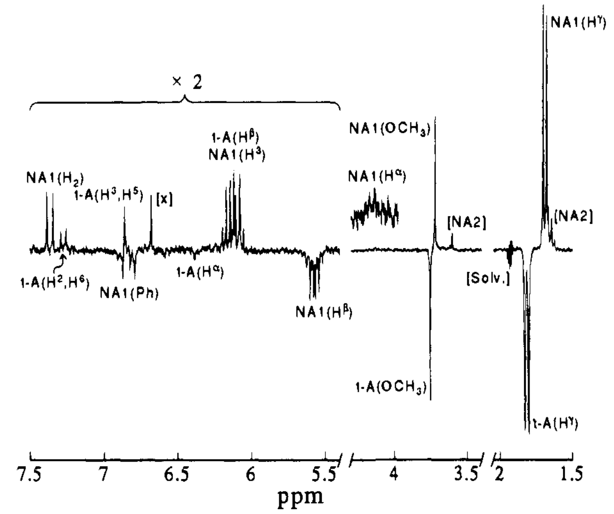

**Figure 1.** Background-free pseudo-steady-state CIDNP spectra observed in the photoreaction of *trans*-anethole *t*-**A** with 1,4-naphthoquinone in acetonitrile-$d_3$ at room temperature. Amplitudes have been multiplied by a factor of 2 in the left half of the spectrum. The assignment of the resonances of the product **NA1** refers to the structural formula of Table 3. For the signals of *t*-**A** see the formula given in Table 2. The signal marked [x] is due to the product of a side reaction; we assign it to naphthohydroquinone.

with quencher concentrations as low as $5 \times 10^{-4}$ M. The primary result of this quenching process is a radical ion pair in a triplet state. For the systems investigated, back electron transfer must be preceded either by intersystem crossing of the pair or by separation of the radicals to give free ions since the reactions yielding $^3$**Q** and **A** or **Q** and $^3$**A** are both too endergonic. For the same reason, triplet–triplet energy transfer from $^3$**Q** to $^3$**A** cannot occur.

The photophysical and thermodynamical considerations with respect to the reactions sensitized by photoinduced electron transfer (i.e., with CNA as an auxiliary sensitizer) will be discussed in the pertaining section.

**Pseudo-Steady-State CIDNP Measurements.** Upon irradiation (357 nm) of *t*-**A** and **NQ** in acetonitrile, strong nuclear spin polarizations are observed (Figure 1) indicating the occurrence of radical pairs in the photoreaction. In addition to the resonances of the starting olefin, new signals appear in the CIDNP spectrum, which belong to photoproducts. By prolonged irradiation, enough of these products can be accumulated to allow their characterization by NMR. A detailed assignment is given below (see Table 3). Two compounds, **NA1** and **NA2**, are formed, which are stereoisomers of the same oxetane. From the intensities of the corresponding CIDNP signals at 1.69 and 1.63 ppm, it is seen that at room temperature **NA1** dominates by far; the yield of **NA2** is about a factor of 10 lower.

When *c*-**A** is used as the starting olefin in place of *t*-**A**, **NA1** is again the major product at room temperature, but no **NA2** is detectable in this instance (see Figure 2). Instead, a small amount of yet another oxetane stereoisomer, **NA3**, is formed, its yield being approximately 15% of that of **NA1** under these conditions. As Figure 2 shows, the temperature has a strong influence on the relative yields of the photoproducts; the ratios **NA2**/**NA1** and **NA3**/**NA1** increase with decreasing temperature. However, the respective isomer that is absent in the high-temperature spectra is also missing[32] at 235 K. A quantitative interpretation of the temperature dependence of the product distribution will be given in the Discussion. From Figure 2 it is further seen that considerable one-way *cis*–*trans* isomerization occurs in these systems. In the CIDNP spectra of *c*-**A**, the methyl protons of the isomerized olefin appear in enhanced absorption,[33] whereas with *t*-**A** as starting material no corresponding signal of the other olefin can be detected.

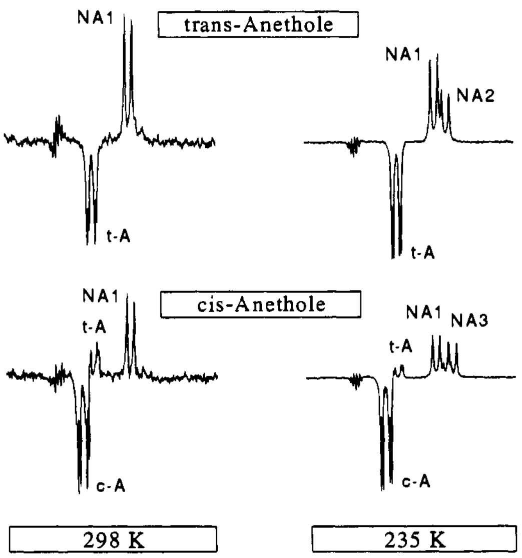

**Figure 2.** Photoreactions of 1,4-naphthoquinone with *cis*- and *trans*-anethole in acetonitrile at different temperatures. The respective starting olefin and temperature are indicated at the traces. The spectra ($1.4 \leq \delta \leq 2.1$) show the CIDNP signals of H$^\gamma$ in the olefins *c*-**A** and *t*-**A** and in the photoproducts **NA1**, **NA2**, and **NA3** (see formulas of Table 3 and Table 2). The minor unlabeled doublet in the low-temperature spectrum of *cis*-anethole is due to a secondary effect.[32]

With **BQ** or **AQ** instead of **NQ**, analogous polarizations are obtained at room temperature (compare Figure 4 below). However, no comparable temperature-dependent product distribution was observed with **BQ**. **AQ**-sensitized experiments at reduced temperature were impracticable because of precipitation of this quinone from the solutions.

The polarization patterns, i.e., the relative polarization intensities of the different protons, reflect the signs and relative magnitudes of the hyperfine coupling constants in the radicals. By comparison of the observed CIDNP patterns with known or estimated coupling constants, the intermediates may thus be identified.[23,24] As Table 2 shows, there is a fairly good correlation between the CIDNP signal intensities of the starting olefin (*t*-**A**) and the hyperfine coupling constants calculated[34] for the *trans*-anethole radical cation. The same polarization

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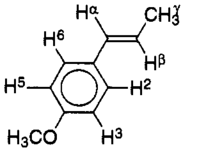
(32) In the CIDNP spectrum of the *c*-**A**–**NQ** system at 235 K (Figure 2), small signals stemming from **NA2** can be seen as shoulders of the two inner lines of the two doublets. However, we attribute these to *t*-**A** present in the *c*-**A** samples. During the CIDNP measurements, some *t*-**A** is formed by one-way isomerization of *c*-**A**, as mentioned in the text. Besides, the *cis*-olefin contains a few percent of the *trans*-isomer as an impurity from the start. The **NA2** signal observed is explained quantitatively by this, as comparison with the intensities of this signal in the other spectrum (*t*-**A**) at the same temperature shows. The average *trans*-content (5–10%) of the *c*-**A** samples necessary for this estimation was obtained from NMR spectra recorded before and after the CIDNP experiment.

(33) In contrast to the NA2 signals in this system (see previous note), these polarizations cannot be explained by *t*-**A** present as an impurity, because this causes an emission signal (compare spectra at the left of Figure 2). As the opposite signals from *t*-**A** regenerated in a cage recombination and *t*-**A** formed by one-way isomerization of *c*-**A** partially cancel, the absorptive polarization and thus the amount of isomerization is actually larger by about 50% than estimated from the spectra.

(34) The magnitudes of the hyperfine coupling constants *a* were obtained by computing the unpaired spin populations $\varrho$ by AM1 with the RHF method and then multiplying $\varrho_i(p_z)$ by $-2.66$ mT (Courtneidge, J. L.; Davies, A. G.; Gregory, P. S. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1527–1532) for the hydrogen atom bonded to sp$^2$-carbon atom *i*, and $\varrho_H(1s)$ by the hyperfine coupling constant of the hydrogen atom (50.7 mT) in the case of the methyl protons. The signs of *a* were determined by an UHF calculation, for which the RHF geometry was used without further optimization.

**Table 2.** Calculated Hyperfine Coupling Constants $a_{calc}$ (in mT) for the *trans*-Anethole Radical Cation and Observed CIDNP Phases of the Respective Protons in the Regenerated Olefin[a]



| H | $\delta$[ppm] | $a_{calc}$ | $-P_{obs}$ |
|---|---|---|---|
| $H^\alpha$ | 6.35 | +0.23 | +(*w*) |
| $H^\beta$ | 6.12 | −0.55 | −(*s*) |
| $H^\gamma$ | 1.81 | +0.49 | +(*s*) |
| $H^2$, $H^6$ | 7.27 | +0.16 | −(*w*) |
| $H^3$,$H^5$ | 6.84 | −0.15 | −(*m*) |
| $OCH_3$ | 3.75 | +0.11 | +(*m*) |

[a] The inverted polarization phases $-P_{obs}$ have been listed because the expression $\mu\epsilon$ sgn $a_i$ sgn $\Delta g$ is negative for this product.

pattern, but with all lines of the corresponding protons inverted, is found for the olefin moiety of the photoproduct **NA1** (compare Figure 1). For reaction systems similar to ours, it has been proposed[26b] that pairs of neutral radicals are formed by proton transfer from the olefin cation to the quinone radical anion within the cage. Such a deprotonation would appear favored as it produces an allyl radical; indeed, the radical cation of triallylamine is known[35] to undergo such a transformation in quinone-sensitized photoreactions. However, our calculations of the hyperfine coupling constants in the respective radical of *t*-**A** indicate that this should lead to quite weak polarizations of $H^\beta$ and very strong polarizations of $H^\alpha$, which is the opposite intensity pattern as observed in our spectra. The same results are found for the other sensitizer/anethole combinations. Hence, we attribute all nuclear spin polarizations in these systems to radical ion pairs.

Further evidence for the absence of polarizations from neutral radical pairs is obtained by experiments in a nonpolar solvent. If toluene is used instead of acetonitrile, no CIDNP can be detected at all, yet products are still formed. As the solvent polarity influences neither the pair dynamics nor the solvation energies of uncharged radicals much and also leaves unchanged their magnetic parameters, this behavior would be difficult to explain if neutral radicals were involved. On the other hand, it would not rule out the intermediacy of radical ion pairs. CIDNP can only be generated during diffusive excursions (separations and reencounters) of the radicals constituting the pairs. In a nonpolar solvent, separation of oppositely charged radical ions is no longer possible owing to their Coulombic attraction; hence CIDNP is suppressed. Such effects have been observed[36] in electron-transfer reactions. However, in our case the reaction proceeds without full charge transfer, i.e., via an exciplex instead of radical ion pairs, in a nonpolar solvent. This is inferred from the different product distributions in acetonitrile and in toluene: in toluene, only **NA1** is formed, even at 230 K, and with both olefin isomers.

Kaptein's rule[37] for CIDNP net effects,

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

relates the polarization phase $\Gamma_i$ of nucleus $i$ ($\Gamma_i = +1$, enhanced absorption; $\Gamma_i = -1$, emission) to the sign of its hyperfine coupling constant sgn $a_i$, sign of the difference of the $g$-values of the two radicals of the pair sgn $\Delta g$, precursor multiplicity ($\mu = +1$, triplet or random phase; $\mu = -1$, singlet), and multiplicity of the radical pair leading to the product observed ($\epsilon = +1$, singlet; $\epsilon = -1$, triplet).[38] We have $\mu = +1$ owing to the triplet multiplicity of the excited quinone. The $g$-value of $\mathbf{NQ}^{\bullet-}$ is 2.0048;[39] that of the anethole radical cations must lie[40] between 2.0040 and 2.00443. With the signs of the hyperfine coupling constants calculated for the anethole cation, we find that the educt olefin is regenerated by back electron transfer of the radical ion pairs in their singlet state, and the oxetane is predominantly formed from triplet radical pairs. This behavior has also been observed[19] in a CIDNP investigation of related systems, e.g., chloranil−indene. By contrast, in another CIDNP study,[20] singlet radical ion pairs were reported as precursors to oxetanes in the photoreaction between chloranil and *N*-vinylpyrrolin-2-one in acetone-$d_6$, but we have not been able to confirm[41] the results of these authors. From the opposite polarization phases of the starting and isomerized olefin in the CIDNP spectra of *c*-**A** (Figure 2), it is evident that one-way *cis−trans* isomerization takes place via triplet radical pairs too, and thus competes with cycloaddition.

The $g$-values of the radical anions of the two other quinones are very similar to that of $\mathbf{NQ}^{\bullet-}$ ($g(\mathbf{BQ}^{\bullet-}) = 2.0050$,[42] $g(\mathbf{AQ}^{\bullet-}) = 2.00443$[43]). As expected, with these sensitizers the same polarization phases are found as with **NQ**.

**Time-Resolved CIDNP Measurements.** Our observation of predominant product formation from triplet radical pairs leaves two mechanistic alternatives. These products may be the result of cage recombination of the triplet pairs to give a triplet species (triplet biradical) which then undergoes intersystem crossing and reacts further. A second possibility would be escape of the radicals from the cage, i.e., loss of spin correlation, and subsequent reactions of free radicals, as has been proposed[19] for the chloranil−indene system. Time-resolved CIDNP experiments[25] ("flash CIDNP") lend themselves well to distinguish between these two pathways, because quite different timescales are involved. Product formation by cage recombination would occur within a few nanoseconds, because intersystem crossing, which is known to be very fast (<10 ns)[4-6]

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(37) Kaptein, R. *J. Chem. Soc., Chem. Commun.* **1971**, 732−733.

(38) Commonly, $\epsilon$ is taken to denote the mode of product formation ($\epsilon = +1$, cage product; $\epsilon = -1$, escape product).[37] The convention (Roth, H. D.; Manion-Schilling, M. L. *J. Am. Chem. Soc.* **1980**, *102*, 4303−4310) adopted here should be preferred, since it includes the other as a special case. Although for many chemical systems the two are equivalent, the usual definition leads to wrong results if cage recombination of triplet pairs is possible, as in our systems.

(39) Alegria, A. E.; Fontanez, F.; Stevenson, G. R. *J. Phys. Chem.* **1976**, *80*, 1113−1117.

(40) In the photoreactions of *c*-**A** or *t*-**A** with fumaronitrile, we observed the same polarization phases of the educt anetholes as in the present work. In that system, the educts are once more regenerated by singlet recombination of an intermediate radical ion pair, but the precursor to the radical pair has singlet multiplicity. Hence $\mu$ is −1, and $\Delta g$ must be negative to account for the observed polarizations. The $g$-values of $c$-$\mathbf{A}^{\bullet+}$ and $t$-$\mathbf{A}^{\bullet+}$ are thus bracketed by the $g$-value of the radical anion of fumaronitrile ($g = 2.0040$: Arnold, D. R.; Wong, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 1894−1895) and the lowest $g$-value of the three semiquinone radical anions, i.e., that of $\mathbf{AQ}^{\bullet-}$.

(41) Upon excitation at 357 nm, we observed very strong nuclear spin polarizations in this system, which were, however, quite different from those shown in ref 20. In particular, we could not find any evidence for the formation of oxetanes under these conditions, neither in the CIDNP nor in the product spectra. We ascribe this disagreement to the unselective excitation with the unfiltered light of a 1000-W high-pressure mercury lamp that was used in ref 20, and we think that the polarizations reported in that study result from photoexcitation and subsequent reactions of another component, presumably the solvent.

(42) Kaise, M.; Nishihara, C.; Nozoye, H.; Someno, K. *Chem. Lett.* **1986**, 589−592.

(43) Sieiro, C.; Sanchez, A.; Crouigneau, P. *Spectrochim. Acta A* **1984**, *40*, 453−456.

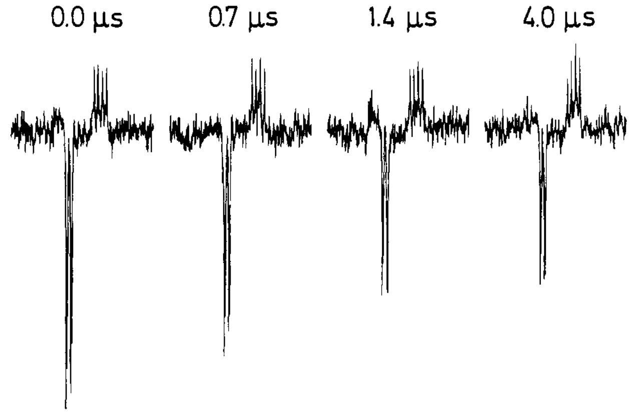

**Figure 3.** Flash-CIDNP measurements of the photoreactions of 1 × $10^{-3}$ M 1,4-naphthoquinone with 4 × $10^{-3}$ M *cis*-anethole in acetonitrile-$d_3$ at 230 K. The delay between laser flash and sampling pulse is indicated at the respective trace. Only the spectral range ($1.3 \le \delta \le 2.2$) encompassing the signals of $H^\gamma$ in the olefins and in the photoproducts (see formulas of Table 3 and Table 2) is displayed.

and lifetime limiting[44] for Paterno-Büchi biradicals,[4-6] is rate determining. In contrast, reactions of free ions must involve bimolecular steps (e.g., reaction of free *t*-**A**$^{\bullet+}$ with free **NQ**$^{\bullet-}$)[45] and thus cannot proceed faster than the diffusion-controlled limit. For small concentrations of radical ions, product formation is therefore expected to be much slower than in the previous case.

In flash-CIDNP experiments with a sample containing 1 × $10^{-3}$ M **NQ** and 4 × $10^{-3}$ M *t*-**A**, we could not detect any time dependence of the CIDNP signal intensities even at 230 K; all polarizations reached a constant level within 100 ns after the laser flash, that is within the limiting time resolution of our spectrometer. From the amount of light absorbed in the active volume of the sample, we calculated a maximum concentration of radical ion pairs of 5 × $10^{-5}$ M. With the Smoluchowski equation[46] that was modified by the Debye factor[47] to take into account the Coulombic attraction between the oppositely charged reactants, we estimated a rate constant for a diffusion-controlled reaction of less than 2 × $10^{10}$ $M^{-1}$ $s^{-1}$ in acetonitrile at this temperature. The first half-life of a bimolecular reaction should thus amount to at least 1 µs, which would be easily detectable with our experimental setup. Hence it is obvious that free radical ions do not contribute significantly to the formation of the oxetane.

Under the same experimental conditions as above, but with *c*-**A** as quencher instead of *t*-**A**, we also observed instantaneous oxetane formation on the timescale of our measurements (Figure 3). However, the pronounced emission signal due to the methyl protons of the starting olefin is seen to decrease immediately after the laser flash, reaching its steady-state level after a time of the order of a microsecond. This can be easily explained by less efficient triplet recombination of the pair *c*-**A**$^{\bullet+}$**NQ**$^{\bullet-}$, which leads to a considerable amount of free radicals *c*-**A**$^{\bullet+}$ escaping from the cage. The nuclear spin polarizations in these free radical cations are exactly opposite to the polarizations in the starting olefin regenerated by cage recombination of singlet radical pairs. Degenerate electron transfer between free *c*-**A**$^{\bullet+}$ and surplus starting olefin transfers these absorptive polarizations to the educt olefin, thus gradually cancelling a fraction of the instantaneously formed emissive signal. This compensation process of CIDNP is well known.[48] No concomitant rise of *t*-**A** is detectable in Figure 3, so no significant *cis*–*trans* isomerization of the free olefin cations takes place within their lifetime. The configurational stability of anethol radical cations has been observed by other authors as well.[49] It is in accordance with our AM1 calculations, which predict an activation barrier for rotation about the cationic double bond of about 80 kJ/mol.

The results of these time-resolved CIDNP measurements clearly demonstrate that the main route leading from the radical ion pairs to the cycloadduct is cage recombination of triplet radical pairs.[50]

**CIDNP Experiments with Photoinduced Electron-Transfer Sensitization.** The results obtained so far do not rule out the occurrence of parallel pathways such that a small amount of spin-polarized products is formed by a side reaction via radical ion pairs, whereas the greatest part of them is produced by reactions involving other intermediates and is thus unpolarized. In particular, direct reaction of an exciplex to a Paterno–Büchi biradical, which is commonly observed in nonpolar solvents and has frequently been proposed for polar solvents as well[1a,7a,9,14-16], would be undetectable by CIDNP as this spectroscopic technique is neither sensitive to exciplexes[23] nor to 1,4-biradicals.[19]

We excluded this possibility by utilizing photoinduced electron-transfer sensitization to generate both partners of the radical ion pairs independently, thus circumventing any cycloaddition mechanism that bypasses charged intermediates. Photoinduced electron-transfer sensitization[51] means using an auxiliary sensitizer to obtain radical ions by photoinduced electron transfer, and then replacing the radical ions of the auxiliary species by the desired radical ions in a dark reaction. In this way, we can ensure that radical ions of the anethole and the quinone are formed without the intermediacy of an exciplex between **A** and **Q**.

9-Cyanoanthracene **CNA** (see Table 1) is a suitable auxiliary sensitizer for the anethole–quinone systems.[52] At 388 nm its extinction coefficient is higher than that of **Q** by a factor of about 500. Singlet–singlet energy transfer from $^1$**CNA** to the anethole is impossible as it is much too endergonic. In contrast, energy transfer from $^1$**CNA** to $^1$**Q** would be thermodynamically feasible, but our experimental results indicate[53] that it can be disregarded. Electron-transfer quenching of $^1$**CNA** by *cis*- or *trans*-anethole is fairly exergonic ($\Delta G^\circ \approx -35$ kJ/mol) and is expected to be diffusion controlled, whereas electron transfer

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

(45) With a more complex mechanism of oxetane formation involving neutral molecules (e.g., via attack of *t*-**A**$^{\bullet+}$ to surplus quinone), charge neutralization must still occur, as the educts are ions and the product is a neutral molecule. Hence, the reaction scheme necessarily contains a bimolecular step between partners that are both present in very low concentrations, which are at most equal to the initial concentration of radical ion pairs.

(46) Smoluchowski, M. V. *Z. Physik. Chem.* **1917**, *92*, 129–168.

(47) Debye, P. *Trans. Electrochem. Soc.* **1942**, *82*, 265–271.

(48) Closs, G. L.; Sitzmann, E. V. *J. Am. Chem. Soc.* **1981**, *103*, 3217–3219.

(49) Lewis, F. D.; Kojima, M. *J. Am. Chem. Soc.* **1988**, *110*, 8664–8670.

(50) In a previous CIDNP investigation[19] of the Paterno–Büchi reaction, it was concluded that the oxetane precursors (biradicals) are formed from escaping free radicals. Polarization phases for this case are the same as for geminate recombination of triplet pairs, so a distinction between these two alternatives is not possible by steady-state CIDNP experiments. It seems possible that the same situation as in our systems is realized in the quinone-sensitized reactions of that work, and that the interpretation of the experimental results of ref 19 may have to be modified accordingly.

(51) (a) Mattes, S. L.; Farid, S. *Org. Photochem.* **1983**, *6*, 233–326. (b) Chanon, M.; Eberson, L. *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.

(52) For photoinduced electron-transfer sensitization in a similar system, see: Brown-Wensley, K. A.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1978**, *100*, 4162–4172.

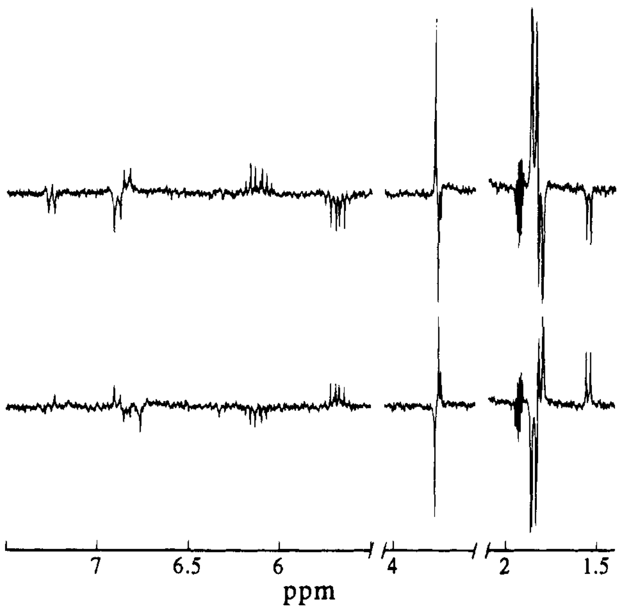

**Figure 4.** Background-free pseudo-steady-state CIDNP spectra observed in the photoreaction of *cis*-anethole *c*-**A** with 1,4-benzoquinone **BQ**. Bottom trace: direct reaction, 1.0 × $10^{-1}$ M **BQ**, 1.3 × $10^{-2}$ M *c*-**A**, optical density of the sample at 388 nm 0.6. Top trace: with photoinduced electron-transfer sensitization by 9-cyanoanthracene (1 × $10^{-3}$ M), 1.3 × $10^{-2}$ M **BQ**, 2.5 × $10^{-2}$ M *c*-**A**, totally absorbing (388 nm) sample. All other experimental parameters are the same in both cases; the spectra have been processed identically and plotted with the same scale settings.

from **Q** to $^1$**CNA** is not possible owing to the high oxidation potential of the quinones.

The life of $^1$**CNA** ($\tau_S$ = 16.9 ns)[54] is sufficiently long to give quenching quantum yields of about 90% with quencher concentrations of 2.5 × $10^{-2}$ M. $\Delta G°$ for the oxidation of the radical anion $\mathbf{CNA}^{\bullet-}$ of the cyanoanthracene by the quinone is highly negative (−50 to −90 kJ/mol), so this reaction should also be diffusion controlled.

Owing to the low-lying triplet state of **CNA** in-cage back electron transfer is feasible for singlet as well as for triplet radical ion pairs, and formation of free ions is expected to be strongly suppressed. This is borne out nicely by experiment. With a sample containing 1 × $10^{-3}$ M **CNA** and 2.5 × $10^{-2}$ M *c*-**A**, no CIDNP could be detected at all, neither in steady-state nor in time-resolved experiments. After prolonged irradiation at 388 nm, no formation of products could be noticed. However, upon addition of 1.3 × $10^{-2}$ M **BQ** to the mixture, strong CIDNP signals were observed that were exact mirror images of the polarizations found in the direct photoreaction, i.e., in the absence of **CNA** (see Figure 4).

By Kaptein's rule (eq 1), the inversion of the polarizations requires the precursor multiplicity to be singlet in this experiment. This militates once more against the participation of free ions (electron transfer between free $\mathbf{CNA}^{\bullet-}$ and **BQ**), because encounters of the resulting free $\mathbf{BQ}^{\bullet-}$ with free $c\text{-}\mathbf{A}^{\bullet+}$ would lead to the same polarization phases as a triplet precursor. The only explanation of the experimental findings is that the initially formed radical ion pair $^{1}\overline{\mathbf{CNA}^{\bullet-}c\text{-}\mathbf{A}^{\bullet+}}$ is intercepted by replacement of $\mathbf{CNA}^{\bullet-}$ by $\mathbf{BQ}^{\bullet-}$ within the cage[55] to give the same radical pair as in the direct photoreaction between the quinone and the olefin, but with singlet multiplicity. Such interception processes have been detected for pairs of neutral radicals by means of CIDNP[56] and have been invoked as explanation for the increased yield of free ions upon photoinduced electron-transfer sensitization with CNA in several systems.[51a,52]

In the CIDNP experiment with the sensitizer **CNA**, there is no possibility of an exciplex $\mathbf{Q}^{\delta-}\cdots\mathbf{A}^{\delta+}$ being precursor to the radical ion pair $\overline{\mathbf{Q}^{\bullet-}\mathbf{A}^{\bullet+}}$. As Figure 4 shows, absolute CIDNP intensities are practically identical in this reaction compared to the direct photoreaction between **BQ** and *c*-**A**, after correcting for the slightly different optical densities of the samples. We also found the product yields to be essentially the same[57] in these two instances. This is clear evidence that a reaction via radical ion pairs is the *main route* for oxetane formation in our systems; a direct conversion of an exciplex into a biradical can be ruled out as a major pathway in acetonitrile.

**Trapping Experiments.** Trapping of several Paterno−Büchi biradicals with oxygen to give 1,2,4-trioxanes[7] or with other scavengers has been reported. However, our experiments with oxygen as a scavenger were unsuccessful. After prolonged irradiation at 235 K of oxygen-saturated (1 bar) acetonitrile solutions containing 2.5 × $10^{-2}$ M of *t*-**A** or *c*-**A** and **NQ**, we did not observe any trapping products. In addition, no new resonances were visible in the CIDNP spectra, which are more sensitive in this case than the product spectra owing to the large signal enhancements by the spin polarizations and would also allow[23] detection of unstable diamagnetic products possessing lifetimes longer than about 500 ms.

**Structure of the Photoproducts.** The photoproducts and their stereochemistry, as inferred from NMR experiments, have been compiled in Table 3. For clarity, chemical shifts and coupling constants of the aliphatic protons have also been included in the table. A complete list of the NMR parameters of the products is available as supplementary material.

From the spectral parameters it is readily deduced that the products are spirooxetanes. Cyclobutane structures, which were found in photocycloadditions of **NQ** to styrene or 4-methoxystyrene in benzene[26b] or for other, similar systems,[26b,58] would be incompatible with the NMR data. For all our photoproducts, an exceptional low-field shift of $H^\beta$ shows that the $\beta$-carbon atom of the olefin moiety is connected to the ring oxygen.

The stereochemistry of **AA**, **BA**, and the high-temperature naphthoquinone−anethole adduct **NA1** was determined by a set of NOE difference experiments (see, for example, Chart 1).[59] These established considerable dipolar interactions between $H^\alpha$,

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(53) Energy transfer from $^1$**CNA** to the quinone would lead to the same CIDNP signal phases as direct excitation of the quinone. As the polarization intensities in the electron transfer sensitized and in the direct reaction are essentially identical, apart from their sign, a significant contribution of singlet−singlet energy transfer appears to be absent in these systems.

(54) Jones, G.; Chiang, S.-H.; Becker, W. G.; Welch, J. A. *J. Phys. Chem.* **1982**, *86*, 2805−2808.

(55) We should like to point out, for clarity, that in the context of CIDNP the concept of a cage does not denote a region of space, but rather a region of time; two radicals belong to a cage as long as their electron spins are correlated, i.e., also during diffusive excursions when they are separated by (possibly many) solvent molecules. Replacement of the auxiliary radical ion ($\mathbf{CNA}^{\bullet-}$) by the desired radical ion ($\mathbf{BQ}^{\bullet-}$) largely occurs during these excursions and not when radical cation and anion are in contact.

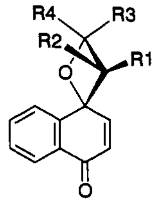
(56) Kaptein, R. In ref 21b, pp 257−266 and references therein. In the context of CIDNP, these interception processes have been termed "pair substitution".

(57) For these systems, product yields may be even higher with photoinduced electron-transfer sensitization than without, because the excitation wavelength can be chosen to overcome unfavorable absorption properties of the products. Hence, we have employed this sensitization method for preparative generation of the oxetanes. A more detailed discussion of radical ion pair interception processes and examples of synthetic applications will be given in a subsequent publication.

(58) Maruyama, K.; Imahori, H. *J. Chem. Soc., Perkin Trans. 2* **1990**, 257−265.

(59) Enhancements below 2% have been omitted from Chart 1. Saturation of $H^\alpha$ was not performed.

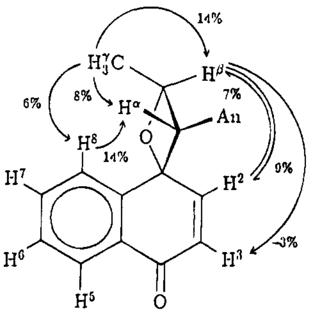
**Table 3.** Structure Assignment of the Photoproducts and Pertinent NMR Data[a]



| compd | educts | R1 | R2 | R3 | R4 | $\delta(H^\alpha)$ | $\delta(H^\beta)$ | $\delta(H^\gamma)$ | $^3J_{\alpha\beta}$ | $^3J_{\beta\gamma}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **BA** | **BQ** + *t*-**A** or *c*-**A** | An | $H^\alpha$ | $H^\beta$ | $CH_3^\gamma$ | 4.04 | 5.41 | 1.55 | 8.5 | 6.1 |
| **AA** | **AQ** + *t*-**A** or *c*-**A** | An | $H^\alpha$ | $H^\beta$ | $CH_3^\gamma$ | 3.90 | 5.65 | 1.71 | 8.5 | 6.1 |
| **NA1** | **NQ** + *t*-**A** or *c*-**A** | An | $H^\alpha$ | $H^\beta$ | $CH_3^\gamma$ | 4.15 | 5.56 | 1.69 | 9.0 | 6.0 |
| **NA2** | **NQ** + *t*-**A** | $H^\alpha$ | An | $CH_3^\gamma$ | $H^\beta$ | 4.21 | 5.63 | 1.63 | 8.5 | 5.9 |
| **NA3** | **NQ** + *c*-**A** | $H^\alpha$ | An | $H^\beta$ | $CH_3^\gamma$ | 4.56 | 5.54 | 1.61 | 9.5 | 6.7 |

[a] Only the spectral parameters for the protons of the oxetane moiety are listed. The stereochemistry of the substituents R1–R4 refers to the structural formula given above the table. An denotes the *p*-anisyl group.

**Chart 1**



$H^\gamma$, and $H^8$, on the one hand, and between $H^\beta$, $H^2$, and $H^3$, on the other. In particular, a three-spin effect was observed at $H^2$ and $H^3$ when $H^\beta$ was saturated, which indicates an approximately linear arrangement of these protons and thus provides further evidence for the structure given.

**NA2** and **NA3**, the low-temperature photoproducts of the anetholes with **NQ**, were found to be rather unstable at room temperature. In particular, **NA3** decomposed within a few hours. Hence we did not attempt isolation of the pure compounds for characterization. Instead, we prepared them *in situ* by irradiation ($\lambda > 395$ nm) of solutions containing $2.5 \times 10^{-2}$ M of the respective educts in acetonitrile-$d_3$ at −60 °C. In this way, we obtained moderately high concentrations of photoproduct mixtures **NA2**/**NA1** and **NA3**/**NA1**, which allowed us to determine the relevant NMR parameters of the low-temperature species.

Chemical shifts and peak splittings unambiguously show that **NA2** and **NA3** are spirooxetanes too. NOE measurements could not to be performed at room temperature owing to the instability of the oxetanes. Furthermore, the spectra of the product mixtures were overcrowded in the aromatic region. Hence, NOE experiments were carried out at −10 °C to slow down decomposition of the products during the measuring time, and only the resonances of the methyl group at the oxetane ring ($H^\gamma$) were saturated. In the case of the *trans*-anethole adduct **NA2**, large NOE enhancements were found solely for $H^\alpha$ (20%) and $H^\beta$. This strongly suggests a *trans* configuration of An and $CH_3^\gamma$, i.e., of the olefin moiety, in **NA2** as well and thus fixes the structure of this stereoisomer. On the other hand, with the photoproduct of *cis*-anethole, **NA3**, no enhancement at $H^\alpha$ could be detected, but an increase of the signal intensities of $H^8$ (23%) and of the ring protons of the anisyl group (10%) was observed. Therefore, we regard a configuration in which $CH_3^\gamma$, An, and the aromatic ring of the quinone part all lie on the same side of the oxetane ring as certain for **NA3**.

Although, taken on their own the coupling constants $^3J$ of the aliphatic protons do not permit an unambiguous determination of the oxetane configurations, they are nevertheless in accordance with the structures proposed. It is known[60] that $^3J_{\mathrm{cis}}$ is larger than $^3J_{\mathrm{trans}}$ in four-membered rings. As Table 3 shows, the largest coupling constant $^3J_{\alpha\beta}$ is found for **NA3**, the only isomer in which $H^\alpha$ and $H^\beta$ occupy *cis* positions. It is further known[61] that $^3J$ crucially depends on the HCC angle, a decrease of this angle leading to an increase of $^3J$. From the table, $^3J_{\beta\gamma}$ is seen to be practically constant for **NA1** and **NA2**, but perceptibly larger for **NA3**. This can easily be explained by noticing that the methyl and anisyl substituents are ecliptic only in the latter. Steric interaction between these groups should cause some deformation such that methyl moves away from anisyl, thus decreasing the valence angle of the $H_3^\gamma C{-}C{-}H^\beta$ fragment and increasing $^3J_{\beta\gamma}$.

Our AM1 calculations gave similar heats of formation (−59, −56, and −46 kJ/mol) for **NA1**, **NA2**, and **NA3**, but the high-temperature product **NA1** is seen to be the most stable one. The distribution of the photoproducts at low temperatures thus does not reflect their thermodynamic stabilities. Within experimental error, the fourth stereoisomer, i.e., $R_1$ = An, $R_2 = H^\alpha$, $R_3 = CH_3^\gamma$, $R_4 = H^\beta$, is not formed at all, although its $\Delta H_f$ (−50 kJ/mol) is essentially the same as that of the other compounds.

## Discussion

**Stage of Isomerization.** It is evident that the configuration of the olefin substituents is retained during formation of the low-temperature photoadducts **NA2** and **NA3**, whereas one-way *cis*–*trans* isomerization of the anethole moiety occurs in the reaction leading to the high-temperature product **NA1**. This isomerization is paralleled by the one-way *cis*–*trans* isomerization of the starting olefin (Figure 2). Moreover, both isomerizations show the same temperature dependence, the yields of isomerized olefin and of **NA1** increasing with temperature and being approximately proportional to each other. It is thus reasonable to assume that these two processes have the same origin and happen at the same stage of the reaction.

Isomerization of the starting olefin is often found accompanying Paterno–Büchi cycloadditions and has been proposed to

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(60) Sternhell, S. *Quart. Rev.* **1969**, *23*, 236–270.

(61) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High Resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959; p 195.

take place via the triplet state $^3$**A** of the olefin[3] or at the stage of the biradical.[14] Isomerization in the radical ions need not be considered, as already pointed out.

$^3$**A** is known[62] to provide a facile route to anethole isomerization, but from the energetic considerations given above it is evident that in our reactions this species cannot be formed at all. Moreover, even if it were possible to populate the triplet state of the olefin, the observed (see Figure 2) one-way *cis*–*trans* isomerization would not be consistent with this intermediate, since $^3$**A** yields almost equal amounts[62] of *c*-**A** and *t*-**A** upon return to the ground state.

In principal, isomerization in a triplet exciplex would also be conceivable. However, this would amount to isomerization before the stage of CIDNP generation, because our experiments with photoinduced electron-transfer sensitization unambiguously show that full charge transfer occurs. Therefore, isomerization in an exciplex would lead to the same polarization phases as a mixture of *cis*- and *trans*-olefin; that is, both the starting and the isomerized olefin would appear in emission, contrary to observation (Figure 2).

Hence, our experimental findings can only be reconciled with isomerization at a later stage of the reaction than the radical ion pair. On the other hand, the oxetanes are configurationally stable under our experimental conditions, so some species capable of geometrical isomerization must go between the radical ion pair and the final product. This clearly rules out direct conversion of the pair to an oxetane, which was proposed in ref 20, but is perfectly consistent with the intermediacy of a biradical as the stage of isomerization.

**Mechanism of Biradical Formation.** For our systems, the CIDNP experiments described have excluded the possibility[4] that radical ions are merely products of a side reaction. Furthermore, our results have furnished direct proof that oxetane formation proceeds neither via radical pairs in the singlet state[10,20] nor via uncorrelated radicals.[19] One group[6] has ascribed the occurrence of radical ions during Paterno–Büchi reactions to a reversible heterolysis of the biradicals that competes with ring closure. However, our conclusion that nuclear spin polarizations are generated before isomerization, i.e., prior to the biradical stage, rules out this pathway too. Instead, our observations are easily rationalized with spin-dependent reactions of correlated radical ion pairs: singlet pairs undergo back electron transfer to regenerate the starting materials, as has already been found in ref 19; triplet pairs combine to give biradicals. The subsequent reactions of these biradicals will be discussed below.

The fact that for singlet pairs electron transfer is preferred to biradical formation is explained by the different distance dependence of these two types of reactions. An electron can be transferred over a range of 7 Å or more,[63] whereas formation of a $\sigma$-bond requires the reactants to be in contact. Hence, if both reactions are allowed, electron transfer is expected to be much more probable than radical combination, because the former may already take place during an approach of two radicals. For the same reason, it has to be considered unlikely that oxetane formation via chance encounters of uncorrelated radical ions to give singlet pairs, as proposed[19] for the cycloaddition of chloranil to indene, could effectively compete with back electron transfer. This is corroborated by our time-resolved CIDNP experiments. Even in the **NQ**–*c*-**A** system, where the spectra (Figure 3) indicate a yield of uncorrelated radical ion pairs in excess of 30%, oxetane formation by this pathway cannot be detected.

The experimentally observed regioselectivity, namely addition of an oxygen atom of the quinone to the $\beta$ carbon of the anethole, is consistent with a reaction of radical ions. According to our calculations, these atoms possess the largest negative and positive charge density, respectively.

**Conformational Changes of the Biradicals.** It is known[44,64] that singlet biradicals are too short-lived for isomerization, whereas triplet biradicals undergo fast internal rotations, thereby relaxing to energetically favorable geometries. Neglecting chirality, the conformations of the biradicals that must precede the products **NA1**, **NA2**, and **NA3** can all be interconverted by rotations around single bonds. Hence the almost exclusive formation of the same cycloadduct, **NA1**, with both anethole isomers at room temperature and the decrease with temperature of the yield of **NA1** in favor of one other stereoisomer, **NA2** or **NA3**, respectively, lead us to conclude that the most stable conformation capable of ring closure is the precursor to **NA1**, whereas the primary product of the combination between $\mathbf{Q}^{\bullet-}$ and $\mathbf{A}^{\bullet+}$ is another biradical with a configuration corresponding to that of **NA2** or **NA3**, depending on the starting olefin.

It is reasonable to assume that the contact radical ion pair, which must be the immediate precursor to the biradical, as well as the transition state leading from this pair to the biradical are stabilized by attractive Coulombic interactions between the oppositely charged olefin and quinone moieties. At the same time, combination of the radicals is expected to be facilitated if the overlap between the $p_z$ orbitals of the atoms forming the new $\sigma$-bond is large. Both Coulombic stabilization and orbital overlap can be maximized if the reactants approach with the quinoid part of $\mathbf{NQ}^{\bullet-}$ and the aromatic ring of the anethole lying face-to-face. The reaction probability should thus be largest for this geometry. It is obvious that the resulting biradical possesses the configuration of the respective low-temperature product (compare Table 3). Such a preorientation of the substrates due to secondary orbital interactions or Coulomb interactions in intermediate exciplexes has been invoked[12,65] to explain the regioselectivity of Paterno–Büchi reactions.

In contrast to the precursor or the transition state, the stabilizing Coulombic interaction between the rings of the quinone and anethole moieties is absent in the biradical, since their opposite charges have been neutralized. Instead, there should be a destabilization of the face-to-face structures that is due to repulsive interactions between filled orbitals.[66] At this stage, a stable configuration in which overlap of the rings is minimized, and, additionally, methyl and phenyl are antiperiplanar, should therefore be preferred. This conformation closely resembles the high-temperature photoadduct **NA1**.

The temperature dependence of the product distribution indicates a small activation barrier for conversion of the initial biradical configuration to the thermodynamically favored configuration. Estimations of these activation energies will be given below. By using molecular frameworks it is seen that a perpendicular orientation of the two orbitals accommodating the unpaired electrons, which is a prerequisite for intersystem crossing in biradicals,[44,67] can be easily attained for all three structures by very small torsional deformations.

The one-way *cis*–*trans* isomerization of the olefin observed in our experiments can be rationalized in the same way, the conformational change of the anethole moiety in the triplet

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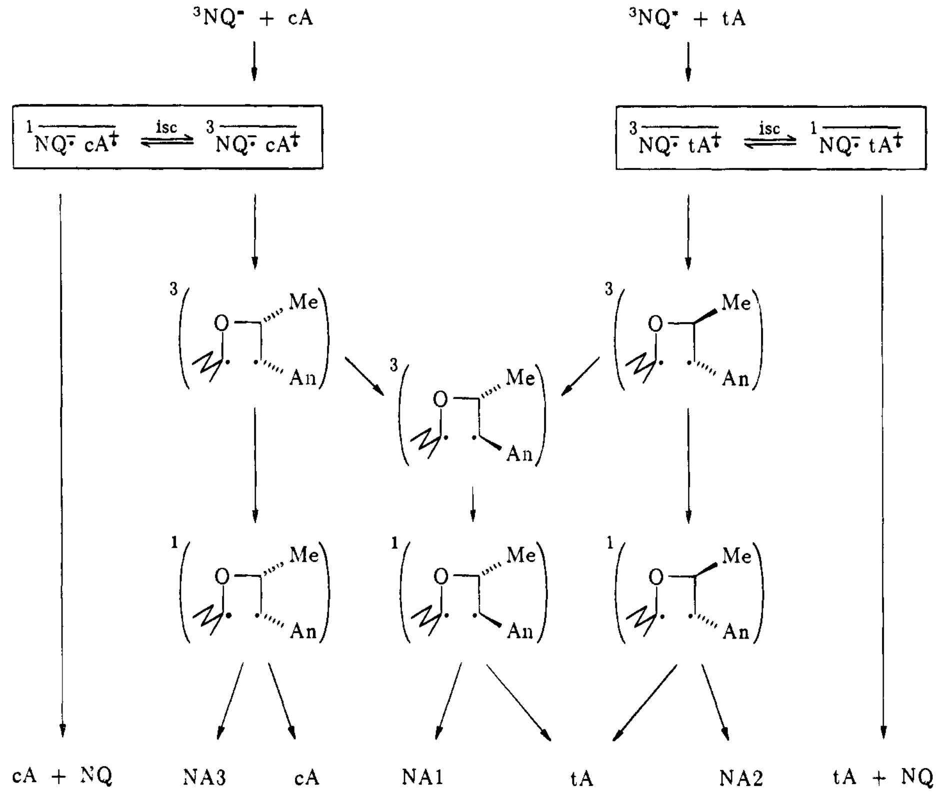
**Chart 2**



biradical to the high-temperature configuration being followed by intersystem crossing and cleavage of the resulting singlet biradical to give the quinone and *trans*-anethole. Since scission of singlet biradicals is a well-known process,[44] this common explanation of both product distribution and one-way isomerization appears very plausible.

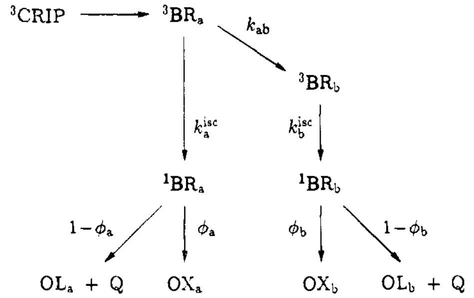
A reaction scheme taking into account all our experimental findings and mechanistic conclusions is displayed in Chart 2. This scheme shows the reactions of **NQ** with both *cis*- and *trans*-anethole but should be applicable to the reactions of other electron-rich olefins with similar sensitizers as well provided that they occur via radical ion pairs. Free ions, which according to our results neither contribute significantly to product formation nor to olefin isomerization, have been omitted for clarity.

With a sensitizer possessing $D_{2h}$ symmetry, as for instance **BQ** and **AQ**, the products corresponding to **NA1** and **NA2** are enantiomers. The fact that we did not observe a temperature-dependent product distribution in the reaction of **BQ** with *t*-**A** is thus in accord with the mechanism given. However, in the reaction of **BQ** with *c*-A at low temperatures the analogue to **NA3** should be formed, which we did not find in our experiments. We attribute this to a lower activation energy for bond rotation in the triplet biradical owing to the smaller size of the quinone moiety.

Finally, the product distribution in the reactions of **NQ** with both anethole isomers in toluene, where the high-temperature product **NA1** is the only result, even at 230 K, indicates that a different mechanism operates in nonpolar solvents, presumably involving exciplexes but certainly not radical ions. It may be of interest for synthetic applications that other stereoisomers of the products are accessible if the Paterno–Büchi reaction proceeds via radical ions, while high regioselectivity is maintained.

**Evaluation of the Temperature Dependence of the Product Distribution.** Bond rotation in the triplet biradicals, which turns the initially formed conformer, the precursor to the respective low-temperature photoproduct, into a more stable conformer, the precursor to the high-temperature product, must be an activated process, as pointed out above. Usually, it is assumed that the equilibrium between the different conformations of a triplet biradical is established during its life, because bond rotation is fast compared to intersystem crossing.[44] However, the fact that besides the common high-temperature oxetane only that low-temperature cycloadduct is formed in which the configuration of the starting olefin is preserved rules out such an equilibration. To simplify the kinetic scheme, we therefore treat the conversion of the initial biradical to the thermodynamically favored conformer as an irreversible process, as has already been done implicitly in Chart 2. Additional support that neglect of the back reaction is justified is provided by the observation that the relative yield of **NA2** or **NA3** becomes very low above room temperature. If the equilibrium between the different conformations were established under these circumstances, lowering the temperature would decrease the equilibrium concentrations of the low-temperature photoproducts still further, since the conversion to the more stable biradical is exergonic. Hence, the back reaction must be correspondingly slow.

**Chart 3**



The kinetic scheme for evaluation of the temperature dependence of the product yields is shown in Chart 3. Geminate recombination of a triplet radical ion pair produces a triplet

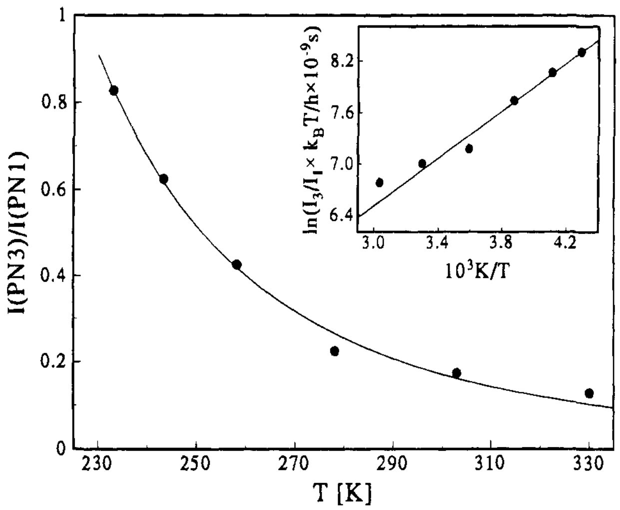


**Figure 5.** Ratio of the CIDNP signal intensities $I$ stemming from H$^\gamma$ (compare Table 3) of the photoproducts **NA3** and **NA1** as a function of temperature. The fit curve and the linearized plot given as inset have been drawn according to eq 3.

biradical in a face-to-face conformation $^3\mathbf{BR}_a$ via a contact radical ion pair $^3$**CRIP**. $^3\mathbf{BR}_a$ can undergo intersystem crossing (rate constant $k_a^{isc}$) to a singlet biradical $^1\mathbf{BR}_a$, which then reacts (relative yield $\phi_a$) to the respective low-temperature oxetane $\mathbf{OX}_a$ or cleaves to give the quinone **Q** and the unchanged educt olefin $\mathbf{OL}_a$. Rotations around single bonds transform $^3\mathbf{BR}_a$ into the more stable conformation $^3\mathbf{BR}_b$ with rate constant $k_{ab}$. Intersystem crossing of $^3\mathbf{BR}_b$ and ring closure of the resulting species $^1\mathbf{BR}_b$ finally leads to the high-temperature photoadduct $\mathbf{OX}_b$; cleavage of $^1\mathbf{BR}_b$ produces **Q** and olefin $\mathbf{OL}_b$. The configuration of $\mathbf{OL}_b$ is *trans* regardless of the configuration of the starting olefin.

From Chart 3 it is obvious that the product ratio $[\mathbf{OX}_a]/[\mathbf{OX}_b]$ is given by

$$\frac{[\mathbf{OX}_a]}{[\mathbf{OX}_b]} = \frac{\phi_a}{\phi_b}\frac{k_a^{isc}}{k_{ab}} \qquad (2)$$

Intersystem crossing rates in biradicals are practically temperature independent.[44,68] Furthermore, we expect that bond rotation does not require a significant activation entropy. Following the Eyring theory, and neglecting the difference between activation energy $E_A$ and activation enthalpy, we thus find

$$\frac{[\mathbf{OX}_a]}{[\mathbf{OX}_b]} = \frac{\phi_a}{\phi_b}\frac{k_a^{isc}}{k_BT/h}\exp\left(\frac{E_A}{RT}\right) \qquad (3)$$

In Figure 5, the experimentally determined ratio $I$(**NA3**)/$I$(**NA1**) of the CIDNP signal intensities of the low-temperature and the high-temperature photoproduct in the system **NQ**–*c*-**A** has been plotted according to eq 3, after correcting for the small *t*-**A** content of the samples (compare footnote 32). From these data, we get an activation energy for bond rotation in the biradical of 11.5 ± 0.7 kJ/mol as a best fit. The same value ($E_A$ = 11.5 ± 1.6 kJ/mol) is found with *t*-**A** as starting olefin. These low activation barriers are not surprising because we are dealing with rotations around $\sigma$-bonds. We regard the fact that for both olefins identical values of $E_A$ are obtained as accidental, since rotations around different bonds, and possibly more than one bond, are involved. Starting from *c*-**A**, the most direct route to isomerization is by rotation around the central bond of the An–C–C–Me fragment. Starting from *t*-**A**, rotation around the $>\dot{\mathrm{C}}$–O bond of the quinone moiety produces the enantiomer of the structure shown in the center column of Chart 3.

By extrapolation to very high temperatures, the preexponential factor in eq 3 can be determined, which in turn allows an estimation of the intersystem crossing rate and thus the life of $^3\mathbf{BR}_a$. As our AM1 calculations indicate the energies of the high-temperature and low-temperature oxetanes to be almost identical, we see no reason why the probabilities of cycloadduct formation should differ strongly for the two singlet biradicals $^1\mathbf{BR}_a$ and $^1\mathbf{BR}_b$. Taking $\phi_a$ and $\phi_b$ to be equal, we thus arrive at a biradical life of 95 ± 35 ps in the case of *c*-**A**. For *t*-**A**, we get a similar result, but with a larger uncertainty (125 ± 80 ps). These values are an order of magnitude smaller than those determined by picosecond spectroscopy[5,6] for other Paterno–Büchi biradicals. On the one hand, these short lifetimes may explain why our efforts to scavenge the biradicals with oxygen failed;[69] on the other, they provide an *a posteriori* justification of our assumption that equilibrium between the different biradical conformations is not established.

Finally, from the CIDNP signals of **NA1** and isomerized olefin in the system **NQ**–*c*-**A**, the yields of ring closure ($\phi_b$) and scission ($1 - \phi_b$) of the singlet biradical in the high-temperature conformation $^1\mathbf{BR}_b$ can be obtained. These show a small temperature dependence: $\phi_b$ was found to be 0.62 at 233 K and 0.49 at 330 K. This trend in the data is in full accordance with expectation, since for entropic reasons higher temperatures should favor biradical cleavage.

## Conclusions

By the CIDNP experiments described, a fairly detailed picture of the Paterno–Büchi reaction between quinones and anetholes in a polar solvent has been provided. The results obtained demonstrate the versatility of this spectroscopic method and show that CIDNP techniques are extremely valuable for the investigation of complex reaction mechanisms, often yielding information that is not accessible otherwise.

All polarizations were found to originate from radical ion pairs. However, as CIDNP is sensitive to radical pairs only, it was necessary to exclude the possibility that the polarizations observed merely stem from a side reaction involving radical ions while the greater part of the products is formed by a parallel process via nonradical intermediates, i.e., a reaction of exciplexes between quinone and olefin to give the biradicals without intervening electron transfer. We ruled this out by using photoinduced electron-transfer sensitization to generate the radical ion pairs indirectly and thus bypass these exciplexes. In these experiments, where the radical pairs are formed with singlet multiplicity, and in the normal photoreactions of the quinones with anethole, where their multiplicity is triplet, we observed mirror image CIDNP spectra with identical absolute values of the polarization intensities of the respective protons. Hence, the pathway that gives rise to CIDNP is the main route of the Paterno–Büchi reaction for the systems studied; full charge transfer occurs and correlated radical ion pairs are central intermediates.

In investigations of reaction mechanisms, preparation of a presumed intermediate by another route is a well-established procedure. Utilization of photoinduced electron-transfer sensitization for the preparation of radical ion pairs in a definite spin state different from the one obtained upon direct excitation and, at the same time, by a well-defined pathway different from the one taken in the normal photoreaction seems an attractive

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(69) A lifetime of triplet biradicals in excess of 1 ns has been reported as a prerequisite for oxygen trapping.[7b]

variety of this technique, especially if CIDNP detection is used.[70] We think that this combination of methods should be applicable, and could prove useful, in other systems as well.

## Experimental Section

**Chemical Substances.** All quinones (Merck) and 9-cyanoanthracene (Aldrich) were purified by repeated sublimation at $10^{-6}$ bar; *trans*-anethole (Aldrich, 99%) was used as received. *cis*-Anethole was prepared from the *trans*-isomer by bromination and subsequent dehydrohalogenation[71] to give 1-phenylpropyne, which was then partially hydrogenated with a nickel catalyst under atmospheric pressure.[72] After spinning band column distillation, the product contained about 5% of the *trans*-isomer, as determined by NMR.

For characterization of the naphthoquinone−anethole adduct **NA1**, a small amount was synthesized by the photoinduced electron-transfer sensitization method described in the Results section. A solution of 220 mg of *trans*-anethole, 300 mg of naphthoquinone, and 50 mg of 9-cyanoanthracene in 50 mL of acetonitrile was irradiated under nitrogen atmosphere with the filtered light ($\lambda > 400$ nm) of a high-pressure xenon lamp (Osram XBO 150 W). When no further turnover was detectable by NMR (after ≈ 15 h), the solvent was evaporated at 20 °C under vacuum. By preparative thin-layer chromatography on $Al_2O_3$ with cyclohexane/ethyl acetate (2.5:1) as eluent, the oxetane was isolated as a yellow oil. After storage at room temperature for several days, considerable decomposition to the starting materials had occurred.

Acetonitrile-$d_3$ (ICB, 99.5% D) was dried over 3 Å molecular sieve before use.

**Sample Preparation.** Sensitizer concentrations were calculated to give an absorbance of the samples at the excitation wavelength of approximately 1. If not stated otherwise, quencher concentrations were chosen to ensure quenching quantum yields of at least 90%. The freshly prepared samples were deoxygenated by bubbling purified nitrogen through the solution and then immediately sealed.

**NMR and CIDNP Measurements.** The NOE measurements of **NA2** and **NA3** were carried out with a Bruker AM-400 NMR spectrometer. All other $^1$H-NMR and CIDNP spectra were recorded on a Bruker WM-250 console connected to a home-made programmable pulse generator. The apparatus was interfaced to an 80 486-based multitasking workstation equipped with a Keithley AD-converter for data acquisition. The optical setup consisted of a two-stage dye laser pumped by an excimer laser, which was triggered by the pulse generator, and a special probe allowing side-on illumination of the samples. A detailed description is found elsewhere.[31,73] The pulse sequences employed for time-resolved[74] and pseudo-steady-state CIDNP measurements[75] have also been described previously. In spectra obtained by these techniques, background signals are strongly suppressed, and intensity errors due to nuclear spin−lattice relaxation in the products are negligible. Excitation wavelengths of 357 nm (RDC-360 neu) or 388 nm (RDC-388) were used for **NQ**- and **AQ**-sensitized or **BQ**- and **CNA**-sensitized experiments, respectively. Actinometric determinations gave energies absorbed in the samples of 1−2 mJ per pulse.

**Calculations.** AM1[76] calculations were performed on an IBM 3090 mainframe computer with the public domain MOPAC 5.0 package.

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**Supplementary Material Available:** NMR parameters of the photoproducts (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[70] A referee pointed out that the idea of preparing the same radical pairs with different multiplicities by chemically different pathways dates back to the early days of CIDNP. For instance, Closs et al. generated benzyl−diphenylmethyl pairs in the singlet state by cleavage of an azo compound and in the triplet state by hydrogen abstraction from toluene by diphenylcarbene (Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1969**, *91*, 4549−4550). These experiments appear related to the present one, although they were never performed with the objective of bypassing a possible intermediate. However, we are not aware of any previous attempt to utilize photoinduced electron-transfer sensitization (pair substitution) in combination with CIDNP detection for that purpose.

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