1.971 Å. At the TCSCF level of theory this latter structure was computed with the 3-21G basis set to be 12.0 kcal/mol above the one in Figure 1a with $r = 1.609$ Å. However, with the six-electron, six-orbital MCSCF wave function the relative energies were reversed, indicating that the MCSCF wavefunction gives an optimal value of r that is considerably larger than that given by the TCSCF wave function.

Since the minimum energy C_{2h} geometry for the 3-21G MCSCF wave function appeared to have an optimal value of r close to that of the SCF wave function ($r = 2.023$ Å), several geometries with fixed values of r in this neighborhood were optimized at the SCF level of theory. Energies were then calculated using the MCSCF wave function; and the minimum MCSCF energy was found to occur at $r = 2.062$ Å. The structure thus optimized is shown in Figure 1b. Its MCSCF energy of −231.6997 hartrees is 14.1 kcal/mol below that of the structure in Figure 1a.

Both the geometry of the MCSCF optimized structure and the fact that the second largest coefficient in the MCSCF wave function is only 0.18 show that this structure is not a diradical. That the structure is, indeed, the transition state in a concerted pericyclic reaction is indicated by the fact that upon simultaneously lengthening one of the two equivalent C–C bonds and shortening the other in 0.01-Å increments, the energy falls smoothly with both SCF and MCSCF wave functions. The MCSCF energy of the transition state is 29.4 kcal/mol above that of 1,5-hexadiene, whose geometry in the all-transoid conformation was optimized at the SCF level. This energy difference is in reasonable agreement with the activation energy of 34 kcal/mol that is measured for the Cope rearrangement.[5]

Our 3-21G MCSCF results provide strong computational evidence that the preferred pathway for the Cope rearrangement of the parent 1,5-hexadiene is via a concerted pericyclic reaction. The reason that a diradical structure is found at lower levels of theory is that the STO-3G basis set and a TCSCF wave function each prejudice the calculations by selectively stabilizing cyclohexane-1,4-diyl relative to two allyl radicals. The single p function used for both σ and π bonds in STO-3G biases this basis set toward the former type of bond, and a TCSCF wave function that correlates the nonbonding pair of electrons in cyclohexane-1,4-diyl provides no correlation for the nonbonding pair in two allyls.

Since cyclohexane-1,4-diyl and two allyl radicals may be viewed as contributors to the resonance hybrid that represents the concerted pericyclic transition state,[14] the correct determination of the lowest energy C_{2h} structure depends critically on the ability of a calculation to describe both these contributors equally well. Otherwise, the result obtained will be biased toward the nonconcerted alternative that is favored by the computational method employed.[15]

Our 3-21G MCSCF finding that the Cope rearrangement proceeds via a concerted pericyclic transition state of C_{2h} symmetry is in disagreement with the previous MINDO results, which found the lowest energy C_{2h} species to be a metastable diradical intermediate.[7] Our 3-21G MCSCF results indicate that in the Cope rearrangement bond making and bond breaking occur in unison, thus also contradicting Dewar's general assertion that multibond reactions cannot normally be synchronous.[8]

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Registry No. 1,5-Hexadiene, 592-42-7.

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[14] Borden, W. T. "Modern Molecular Orbital Theory for Organic Chemists"; Prentice-Hall: Englewood Cliffs, NJ, 1975; pp 129–131.

[15] Similarly, an SCF calculation would be biased toward finding a concerted pericyclic pathway, since diradicals cannot be adequately described with a single-determinantal wave function. Because both diradical contributors to the resonance hybrid for the concerted transition state are described equally poorly with an SCF wave function, the optimal C_{2h} geometry at the SCF level is similar to that found at the MCSCF level, where both contributors are described equally well. Nevertheless, the poor description at the SCF level of the diradical contributors to the transition state results in the calculated energy of activation being 12.3 kcal/mol higher at the SCF than at the MCSCF level of theory.

Energetics and Dynamics of Radical Pairs in Micelles. Measurement of the Average Singlet–Triplet Energy Gap by means of the Magnetic Field Dependence of ^{13}C CIDNP

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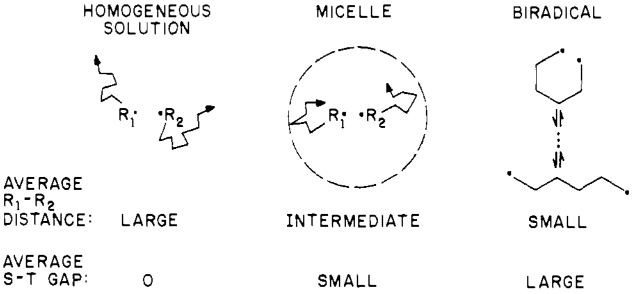
Among species with homolytically broken bonds, radical pairs and biradicals occupy opposite structural and dynamical extremes, as illustrated below.



The radical fragments of a geminate pair are free to diffuse independently in solution, but the two ends of a biradical are severely constrained. Intuitively one expects that radical pairs generated within a micelle occupy a position intermediate between these two extremes. Several aspects of the chemistry of radical pairs in micelles have in fact been found to be unique to the micellar medium.[1] What is lacking is a structural/dynamical scale that allows a quantitative measure of the position occupied by radical pairs in micelles. We wish to report the first such measurements.

A reasonable definition for such a scale is the singlet–triplet energy gap E_{ST}, and the easiest way to measure it is by the magnetic field dependence of CIDNP.[2-4] For radical pairs in homogeneous solution E_{ST} is typically zero.[2b] For biradicals E_{ST} is nonzero and can be either positive (triplet ground state) or negative (singlet ground state).[3] The above diagram illustrates the approximate inverse relation between E_{ST} and the spatial separation of the radical centers. In biradicals there is experimental[3b-d] and theoretical[5] evidence that other factors, such as through-bond coupling and the mutual orientation of the two ends, strongly affect E_{ST}.

Consider a biradical with $E_{ST} < 0$. In an external magnetic field the triplet sublevels T_{+1}, T_0, T_{-1} are split by the Zeeman energy while E_{ST}, the energy difference between the S and T_0 states, is unaffected. If we adjust the magnetic field to produce a T_{-1}–S degeneracy the intersystem crossing rate—and hence the CIDNP intensity—will exhibit a local maximum[2-4] at this field

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[1] (a) Turro, N. J.; Anderson, D.; Chow, M.-F.; Chung, C.-J.; Kraeutler, B. *J. Am. Chem. Soc.* **1981**, *103*, 3892. (b) Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Kraeutler, B. *Ibid.* **1981**, *103*, 3886. (c) Turro, N. J.; Mattay, J. *Ibid.* **1981**, *103*, 4200.

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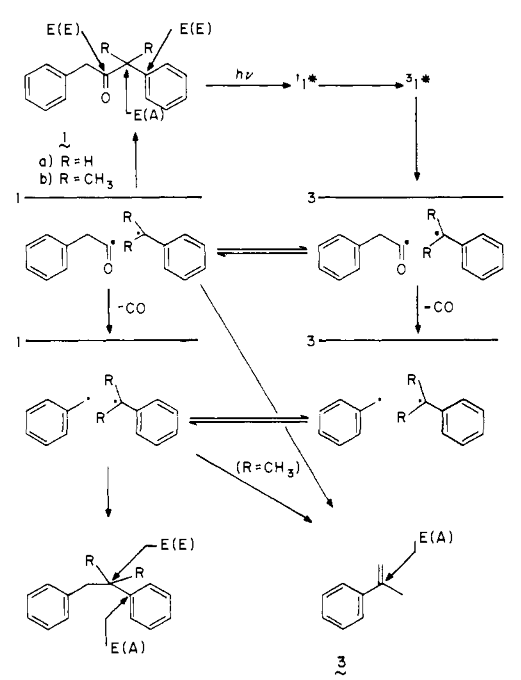

Figure 1. Mechanistic scheme for dibenzyl ketone photolysis. Micellar CIDNP for individual ^{13}C nuclei are displayed (*A* for absorption, *E* for emission) at low field, with high-field CIDNP in parentheses.

strength, H_{max}. Therefore, a field dependence (fd) plot of CIDNP intensity vs. magnetic field gives the average $|E_{ST}|$ equal to $g\beta H_{max}$.[6] It also gives the sign of E_{ST},[2-4] since CIDNP selection rules require emission (absorption) from all polarized nuclei as a result of T_{-1}–S (T_{+1}–S) mixing in the biradical, regardless of the sign of the electron–nuclear hyperfine coupling constant *A*. Predominant T_{-1}–S mixing implies $E_{ST} < 0$ and T_{+1}–S mixing implies $E_{ST} > 0$.

^{13}C CIDNP fd curves were generated by photolysis of micellar solutions of dibenzyl ketones in an auxilliary electromagnet, with the photolysis chamber connected via a recirculating flow system to the spinning sample tube of a Bruker WP-80 FTNMR spectrometer. Figure 1 summarizes the chemistry involved and shows the micellar CIDNP phase at low and high field. Photolysis of 0.0004 M **1a**, 90% enriched in the carbonyl position, in aqueous sodium alkyl sulfate micelles produced strong emission in the carbonyl of **1a**. Figure 2 shows the fd curves generated in 0.21 M sodium octyl sulfate (SOS), 0.07 M sodium decyl sulfate (SDeS), and 0.07 M sodium dodecyl sulfate (SDS). Natural abundance **1a** was also examined at low and high field in micellar and homogeneous media. At 290 G, photolysis of 0.005 M **1a** in 0.07 M SDS produced emission in the carbonyl carbon of **1a** ($A > 0$ in the radical pair) and in the quaternary ring carbons of **1a** ($A < 0$) and of **2a** ($A < 0$). Photolysis of 0.3 M **1a** in methanol at 290 G produced absorption in the carbonyl and ortho and para ring carbons of **1a**, in accord with Closs's low-field rules,[2b] while the CIDNP of **2a** was opposite to Closs's rules. The interpretation here is complicated by the large number of proton couplings.[2b] At 14 kG in both SDS and methanol the CIDNP obeyed Kaptein's T_0–S rules[7] (Figure 1). Photolysis of 0.0004 M **1b**, 90% enriched at the quaternary benzylic position, between 25 and 1000 G in 0.07 M SDS produced emission of the labeled position in **1b**, **2b**, and **3b**, with a maximum intensity at 75 G. The high-field CIDNP (Figure 1) obeys Kaptein's rules.[7]

We interpret the low-field micellar CIDNP to be the result of predominant T_{-1}–S mixing in radical pairs having, on average, a singlet ground state. The H_{max} values of Figure 2 correspond to a matching of the T_{-1} and S spin levels and are approximately equal to $|E_{ST}|$ averaged over the lifetime of the radical pair.[6] H_{max} is 365 ± 25 G (0.034 cm^{-1}) in SOS, 325 ± 25 G (0.030 cm^{-1}) in SDeS, and 275 ± 25 G (0.026 cm^{-1}) in SDS.

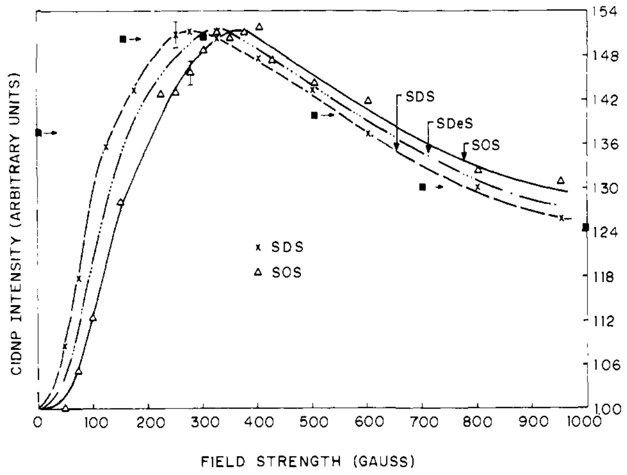

Figure 2. CIDNP fd curves for the emission line of the carbonyl carbon of **1a** produced by photolysis of **1a** in SOS, SDeS, and SDS, normalized to the same maximum value. To avoid congestion only the SOS (Δ) and SDS (×) experimental points are shown with representative error bars. The α fd curve (squares, right vertical axis) is taken from ref 1a.

This interpretation rests on the following evidence: (1) The natural abundance CIDNP of **1a** shows emission independent of the sign of *A*. This requires T_{-1}–S mixing as the predominant source of CIDNP. Closs's analysis of low-field CIDNP[2b] requires that if $E_{ST} = 0$, nuclei with opposite signs of *A* give opposite CIDNP. Since this is not observed, $E_{ST} \neq 0$, and T_{-1}–S mixing implies $E_{ST} < 0$. (2) Changing from micellar to homogeneous media produces completely different CIDNP at low field but identical CIDNP at high field. In methanol at low field the CIDNP depends on the *sign* of *A*, and for **1a** we obtained the result predicted by Closs[2b] when $E_{ST} = 0$. (3) The relation between surfactant chain length and H_{max} is in striking agreement with the relation between biradical chain length and H_{max} in type I photolysis of cycloalkanones.[2a] For SOS, SDeS, and SDS the aggregation numbers are 27, 41, and 64, respectively.[8] Over its lifetime a radical pair is expected to explore a greater volume and experience a greater average separation and, therefore, a smaller average E_{ST} (smaller H_{max}) on changing from SOS to SDeS to SDS. Figure 2 documents this effect and provides the first quantitative measure of it.[9]

Interpreting Figure 2 in terms of a T_{-1}–S crossing resolves a puzzling feature of the ^{13}C magnetic isotope effect on photolysis of **1a** in micellar media.[1a] As measured by the single-stage enrichment parameter α, photolysis of **1a** in hexadecyltrimethylammonium chloride micelles gives significant ^{13}C enrichment in the carbonyl position of **1a**. Figure 2 shows that the magnetic field dependence of α[1a] qualitatively matches the ^{13}C CIDNP fd curves.[10] The simplest explanation is that all maxima of the curves in Figure 2 arise from the same phenomenon: an energy matching

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[6] (a) The exact zero-order E_{ST} includes a contribution of *A*/4 from the hyperfine interaction. At low field the diffusive dynamics of the radical pair can also affect the value of H_{max}, though it remains dominated by E_{ST}. (b) We expect no contribution to H_{max} from the zero-field splitting, since it is averaged to zero on a shorter time scale than the development of CIDNP.

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[9] (a) For comparison the 1,11- and 1,12-biradicals generated from type I cleavage of cycloundecanone and cyclododecanone have H_{max} = 400 and 290 G, respectively (vide supra, ref 2a). (b) A referee has suggested that nuclear cross-relaxation in the products, presumably involving ^{1}H and ^{13}C, may account for the CIDNP. Polarization transfer from ^{1}H to ^{13}C is an unlikely source of the completely emissive CIDNP. Kaptein has shown that polarization must be transferred with inversion of CIDNP phase for radicals of the size considered here (Hore, P.; Egmond, M.; Edzes, H.; Kaptein, R. *J. Magn. Reson.* **1982**, *49*, 122). Closs's[2b] low-field rules predict *E* for the benzylic protons of **1a**. This requires an *A* phase for ^{13}C nuclei coupled via cross-relaxation, contrary to our observations.

[10] Note that α and CIDNP were measured in different surfactants. Measurements under identical conditions are planned, but even then one would not expect the α and CIDNP fd curves to coincide exactly, since they measure different properties.

of the T_{-1} and S spin states. The T_{-1}–S degeneracy produces a local maximum in the CIDNP intensity and also in the total intersystem crossing rate, to which α is sensitive. Thus the biradical character (nonzero E_{ST}) imposed on a radical pair by a micellar environment has practical applications in the area of ^{13}C enrichment. The magnetic field dependence of CIDNP then becomes a useful predictive tool for this purpose.

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Registry No. 1a, 102-04-5; **1b**, 6304-68-3; SOS, 142-31-4; SDeS, 142-87-0; SDS, 151-21-3.

"Spin–Charge Exchange" in a Stable Radical-Carbenium Ion

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The *inert free radicals* are trivalent carbon species which not only do not dimerize and do not react with oxygen but are inert even toward aggressive chemicals, such as concentrated sulfuric acid, concentrated nitric acid, chlorine, bromine, etc.[1] Their half-life times in solution, in air, are of the order of 100 years. They also withstand temperatures up to 300 °C in air without significant decomposition. They possess therefore a general stability higher than that of an overwhelming majority of "normal", tetravalent carbon compounds and materials. In contrast, they are active in certain one-electron-transfer processes giving stable, isolable carbanion[1a,2] and carbenium ion[1e,3] salts.

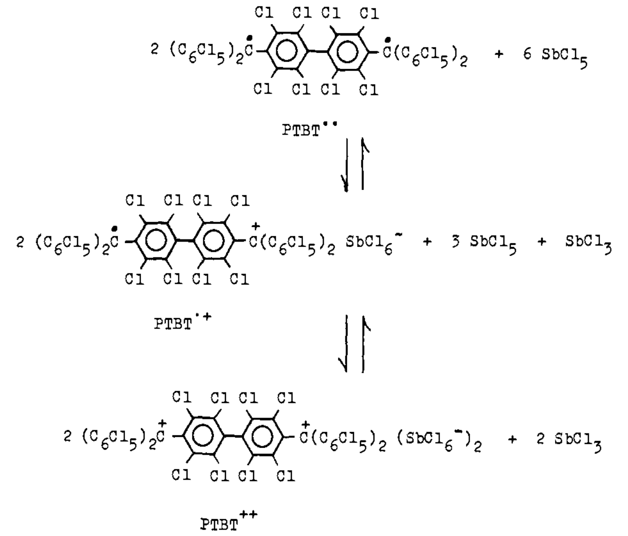
The oxidation of inert radical perchlorotriphenylmethyl (PTM·) with $SbCl_5$[1e,3] takes place according to the equilibrium

$$\underset{\mathrm{PTM}\cdot}{2(C_6Cl_5)_3C\cdot} + 3SbCl_5 = \underset{\mathrm{PTM}^+}{2(C_6Cl_5)_3C^+}\ SbCl_6^- + SbCl_3$$

The preparation of pure perchlorotriphenylcarbenium (PTM^+) hexachloroantimonate can easily be performed by using a great excess of $SbCl_5$ in CH_2Cl_2, with or without added chlorine, or in sulfuryl chloride. Conversely, this salt reverts to PTM· with $SbCl_3$. When the stoichiometric amount of $SbCl_5$ is employed a mixture of PTM· and PTM^+ is obtained.

A remarkable inert carbon diradical is perchloro-$\alpha,\alpha,\alpha',\alpha'$-tetraphenylbi-*p*-tolyl-α,α'-diyl (PTBT:)[1a] and analogously it reacts with a stoichiometric proportion of $SbCl_5$ (in CH_2Cl_2, at room temperature) affording two coupled, balanced equilibria, the components being PTBT:, perchloro-$\alpha,\alpha,\alpha',\alpha'$-tetraphenylbi-*p*-tolyl-α,α'-diylium (PTBT^{2+}) ion, and perchloro-$\alpha,\alpha,\alpha',\alpha'$-tetraphenylbi-*p*-tolyl-α-yl-α'-ylium ($\mathrm{PTBT}^{+\cdot}$) ion.

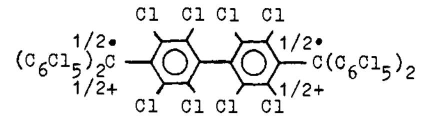
With use of a great excess of $SbCl_5$, an excellent yield of salt $\mathrm{PTBT}^{2+}\ 2SbCl_6^-$ is obtained in form of green-blue crystals. This oxidation is followed by the ESR technique, and when the diradical PTBT: has disappeared, the spectrum of *pure* radical–cation $\mathrm{PTBT}^{+\cdot}$ can be observed, although it decays because of conversion to PTBT^{2+}.



Under similar conditions, the same equilibrium mixture is obtained by an *one-electron-transfer process* between PTBT: and PTBT^{2+}.

$$\mathrm{PTBT}: + \mathrm{PTBT}^{2+} = 2\mathrm{PTBT}^{+\cdot}$$

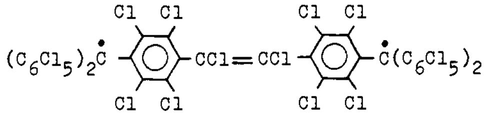
The ESR spectrum of radical–cation $\mathrm{PTBT}^{+\cdot}$ (Figure 1, curve a) indicates a fast "spin–*charge exchange*". Its existence, as inferred from the ^{13}C couplings, is straightforward and unequivocal on account of the absence of interfering nuclei and the simplicity of its hyperfine structure—as it occurs in other perchloro free radicals.[1] Table I reports the coupling constants with the α, bridgehead, and ortho ^{13}Cs for both the radical–cation $\mathrm{PTBT}^{+\cdot}$ and monoradical PTM·. The data indicate that the *spin* densities at the nuclei in $\mathrm{PTBT}^{+\cdot}$ are half as high as in PTM· (Figure 1, curve b).



$\mathrm{PTBT}^{\cdot+}$

It is noteworth that such an exchange takes place in spite of the severe steric inhibition of resonance due to the *quasi*-perpendicularity of two benzene rings in the biphenyl system as it occurs in PTBT:[1a] and perchlorobiphenyl (~87°).[4]

It is pointed out that diradical PTBT: *does not* show a *spin–spin* exchange,[1a] while vinylene diradical **1**, because of lower steric inhibition,[1c] does (half-normal ^{13}C couplings). The ultraviolet-visible spectrum of PTBT: is practically coincident with that of radical PTM· indicating that, within the relevant time scale, the former behaves also as two electronically independent moieties.[1a]



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The characterization, the yields, and the structural assignment of the salts here reported have been performed by hydrolytic conversion[1e] into their fuchsonoid derivatives (perchloro-α'-(4-oxocyclohexadienylidene)-α,α,α'-triphenyl-bi-*p*-tolyl-α'-yl radical and perchloro-α,α'-bis(4-oxocyclohexadienylidene)-α,α'-di-

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