ESR detection of spin-polarized short-lived biradicals has been shown to be a valuable tool in studying the mechanisms of photochemical reactions and in the investigation of the properties of biradicals. However, some important spectroscopic features of these species are not readily available because of certain peculiarities of biradical ESR spectra. This difficulty can be overcome through the conservation of spin polarization by the controlled scavenging of a biradical into a subsequent radical species whose spectroscopic features can be accurately evaluated. In particular, it is shown that the hyperfine splittings of a radical site in a biradical can be measured directly by time-resolved ESR if the other site is scavenged by a selective spin trap. BrCCl₃ was used as a selective scavenger of the acyl moiety of polymethylene linked acyl-alkyl and acyl-benzyl biradicals formed in the photolysis of substituted cycloalkanones in solution. Transformation of these polarized biradicals into corresponding polarized monoradicals upon bromine abstraction by acyl site leads to much less complicated and much better resolved ESR spectra. The hyperfine splittings of the benzylic termini of several acyl-benzyl biradicals generated in this manner were evaluated and quantitatively compared with the splittings of benzyl and 1-phenylpropyl radicals formed in the...
photolysis of linear ketones.
Determination of Hyperfine Splittings of Biradical Termini by Combining Biradical Trapping and Time-Resolved ESR Techniques

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Introduction

Transient biradical species have been the subject of considerable interest for quite a long time.1 Spin trapping is a commonly employed technique to establish the identity of biradicals and to evaluate such parameters as their lifetimes2 and even singlet-triplet splittings.4 Biradical scavenging was also shown to alter the relative yields of intramolecular products2,3 and even singlet-triplet splittings.4 Biradical scavenging was also shown to alter the relative yields of intramolecular products2,3 and even singlet-triplet splittings.4

Paramagnetic scavengers, such as free radicals9-11 or molecular oxygen,3 are able to assist intersystem crossing in biradicals. However, reactions of diamagnetic quenchers with biradicals often resemble those with the corresponding monoradicals.12,13 Thus, the result of scavenging of biradicals by diamagnetic scavengers can usually be predicted if the reactivity of monoradical analogs is known.

Until recently, the direct observation of biradicals by electron spin resonance (ESR) spectroscopy was successful only under conditions which made biradicals relatively stable, e.g., by the matrix isolation technique.14 The development and application of direct detection time resolved ESR (TR ESR) has allowed the thorough investigation of the ESR spectra of short-lived polymethylene linked acyl-alkyl and bis(alkyl)biradicals formed in the photolysis of methyl substituted cycloalkanes.15-17 In particular, the parameters for exchange interaction of electron spins for biradicals of different chain lengths including the cases with restricted chain flexibility were evaluated.18 The relative contributions of through-bond and through-space couplings in biradicals are also issues of current interest.19

To clarify further the mechanisms of exchange interaction and to refine the exchange parameters extracted from the simulations of TR ESR spectra, it is useful to investigate a range of biradicals of different structures.20 As an extension of investigating their photochemistry, we are currently studying the polarized ESR spectra of acyl-benzyl and bis(benzyl) polymethylene linked biradicals formed in the photolysis of 2-phenyl- and 2,4-diphenyl-cycloalkanes by the TR ESR technique.

Experimental Section

1-Phenyl-2-butane, spectrograde or HPLC grade benzene (Aldrich), and triacetin (Janssen Chimica) were used as received.

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Acyl radicals are known to efficiently abstract bromine from BrCCl₃. Since in many cases the reactivity of biradical sites and the same sites in monoradicals is very similar, as, e.g., in hydrogen atom abstraction from mercaptans, BrCCl₃ is expected to serve as an efficient scavenger of the acyl terminus of biradicals such as the one shown in Scheme I. Moreover, the rate constant for reaction of a benzyl radical center with BrCCl₃ is expected to be orders of magnitude smaller than for reaction of the acyl terminus with BrCCl₃. The rate constants reported for similar radicals are $2.2 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$ for benzyl radical at room temperature²⁷ or $1.07 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$ for benzyl (room temperature⁴⁴) and $2 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$ for 1-phenylethyl radicals (80 °C⁴). Thus, proper control of the concentration of BrCCl₃ is expected to allow the selective scavenging of the acyl terminus of acyl-benzyl biradicals. A qualitatively similar situation should pertain to the scavenging of acyl-alkyl biradicals.

Thiols³⁸ and BrCCl₃⁴-⁶ have been used as biradical scavengers to induce nuclear polarization (CIDNP) or to enhance $^{12}C/^{13}C$ isotope separation in the products of cycloalkanone photolysis. These results, together with the NMR product analysis in the experiments with $^{13}C$ labeled compounds,⁹ suggest that in the presence of BrCCl₃ the acyl–benzyl biradical (Scheme I) is transformed into a radical pair (RP) of substituted benzylic and CC₁ radicals as a result of Br atom abstraction by the acyl terminus. Preliminary ESR results²⁹ support this assumption. As shown below, the elimination of biradical nature of the intermediates produced by photolysis of a series of ketones in the presence of BrCCl₃ leads to ESR spectra of the corresponding monoradicals with well-resolved hyperfine structure. The ketones and corresponding radicals studied are shown in Scheme II.

To test the proposed approach, consider (Scheme II) the photolysis of 2,2,12-trimethylcyclodecane (1) which yields the radical (2). The latter possesses two sets of equivalent nuclei with relatively large HFC constants that are expected to make its ESR spectrum simple and unambiguous. In addition, the HFCs for a variety of alkyl radicals under different conditions reported in the literature²⁶ can be used for comparison and as a check of the validity of the proposed approach. The spectrum detected when I was photolyzed in the presence of 17 mM BrCCl₃ is shown in Figure 2a. Although a higher reactivity is expected for the acyl radical center toward BrCCl₃, alkyl radicals are also known to react with BrCCl₃,³¹ so a certain amount of the alkyl terminus is probably scavenged. Indeed, at higher BrCCl₃ concentrations (≥45 mM) the ESR signal disappears completely. This demands that the signal be detected at relatively short delays after the laser flash and leads to line broadening in the observed spectrum. Strong electron spin polarization observed (low field in emission, high field in absorption, E/A) is essential in CW TR ESR experiments to achieve good sensitivity and is fortunately often the case for photolytically generated short-lived radicals. It is interesting to note, however, that polarization possessed by radical (3) and other radicals formed in similar reactions is generated in the preceding biradical, with polarization generated in secondary pairs by RPM being considerably smaller. This fact combined with fast relaxation of CCl₃ radicals can explain why the latter is not observed in the spectrum of Figure 2a and other spectra reported here. Detection of CCl₃ radical by TR ESR has been reported for systems involving either strongly polarized radicals³² or high concentrations of equilibrated CCl₃ radicals.²²

Comparison of the experimental spectrum with the simulated spectrum (Figure 2b) shows some differences of relative line intensities in the central portion of the spectra. This is probably due to some triplet mechanism (TM) net absorptive contribution to the experimental spectrum (E/A* pattern is observed) and is similar to the case of di-tert-butyl ketone photolysis.²² The HFC constants obtained from the simulation ($\alpha(CH) = 22.88 \pm 0.1$ G, $\alpha(CH) = 18.10 \pm 0.15$ G) are somewhat different from those

**Results and Discussion**

Scheme I illustrates the relevant processes, initiated photolytically, in the case of 2-(p-tert-butylphenyl)cycloalkanone: they are common to all the cyclic ketones studied. Upon photolysis, the ketone, after intersystem crossing from the excited singlet state, undergoes a-cleavage from its triplet state and forms a triplet acyl–benzyl biradical (BR, Scheme 1).²⁻²³ The latter possesses a characteristic ESR spectrum (Figure 1) which displays alternating emissive and absorptive lines.²⁴ The spectrum is asymmetric due to the difference in g-factors of the two radical sites. The ESR lines are broadened and shifted as compared to the spectra of corresponding monoradicals (cf. Figure 3) as a result of an interaction of the two unpaired electron spins. Thus, for ESR spectra of biradicals, especially those possessing an acyl radical terminus, it is almost impossible to measure the hyperfine splittings directly and accurately.

**Scheme I**

The syntheses of 2,2,12-trimethylcyclodecane and 2-phenylcycloalkanones have been described previously.²⁻²³ 4-Phenylhexan-3-one was synthesized by alkylating 1-phenyl-2-butanol using KF and C₂H₅NH in THF and was purified by column chromatography on silica gel (hexanes and ethyl acetate eluting solvents). Capillary GC, GC/MS, IH, and $^{13}C$ NMR were used to characterize the products. No evidence of any compound with alkylation at the 3 position was observed.

Typically, a 10–15 mM solution of ketone in benzene was employed. 2-Phenylcycloalkanones were photolyzed in the presence of 45 mM BrCCl₃. For 2,2,12-trimethylcycloalkanone, 17 mM BrCCl₃ in benzene was added to a 90 mM solution of the ketone. After purging with argon for 20 min the solutions were photolyzed (308-nm light (XeCl) of a Lambda Physik EMG 100 excimer laser) in a quartz flow cell (1-mm thick) positioned in the rectangular cavity of an X-band ESR spectrometer (Bruker, ER 100D). Direct detection of ESR signals without magnetic field modulation was employed. The output of the MW bridge broadband preamplifier (6.5 MHz) was fed into the boxcar averager and signal processor (PAR, Models 4420 and 4402). Operations of the laser and the boxcar were synchronized using the output of a fast photodiode as a triggering signal for the boxcar averager. The estimated deadtime for this configuration is ca. 200 ns and is taken into account in the integration windows indicated in the figure captions. Note that the CW TR ESR spectra are detected as true absorption and emission signals unlike conventional first derivative spectra in experiments with magnetic field modulation. Further details of the experimental setup have been described elsewhere.²²

FT ESR spectra were detected employing a Bruker ESP-380 pulsed ESR spectrometer equipped with a 1 kW TWT amplifier (90° pulse length—16 ns) with a LeCroy 9450A oscilloscope as a fast digitizer (400 Ms/s sampling rate). The solutions were either static or flowing through a 4 mm o.d. quartz cylindrical cell.

A pulsar program was written for ESR spectra simulations. A conventional $^{1}Q^{1/2}$ dependence of line intensities was used²⁻²⁴ with Q being the $S-T_m$ mixing frequency. The contribution of only one of the two radicals in a radical pair RP is retained, since one radical usually prevails in the experimentally observed spectra. The lines in the calculated spectra have a Lorentzian shape with the same full width at half maximum (fwhm). In certain cases a three-point smoothing of the recorded spectra was used for clearer presentation, while the original spectra were used for simulations.
Figure 1. Experimental ESR spectrum of biradical (BR) (Scheme 1) obtained during the photolysis of ketone (5su) with an integration window 0.2-0.5 μs after the laser flash.

Figure 2. (a) Experimental ESR spectrum of radical (2) obtained during the photolysis of ketone (1) in the presence of BrCCl₃ with an integration window 0.4-0.9 μs after the laser flash. (b) Simulated spectrum. Lines have Lorentzian shape with fwhm = 1.2 G. HFC constants determined are A(CH₃) = 22.88 ± 0.1 G, A(CH₂) = 18.10 ± 0.15 G.

Figure 3. (a) Experimental ESR spectrum of radical (6SU). Integration window 0.7-1.2 μs. (b) Simulation: lines are assumed to have Lorentzian H shape with fwhm = 0.9 G. The HFC constants determined are shown in Table I.

for 2-methylpent-2-yl radical [A(CH₃) = 22.2 G, A(CH₂) = 17.8 G]. Despite these differences the comparison leaves no doubt about the assignment of the experimental spectrum to the radical 2. This result supports the reaction mechanism of Scheme I and demonstrates that the proposed approach can indeed provide the information about hyperfine splittings of interest.

In the case of 2-phenyl substituted cyclic ketones (3, 5R, and 5PD, Scheme II) the variation of scavenger concentration in the range 8 mM-1 M does not lead to significant changes in the spectra observed, indicating a much smaller rate of Br atom abstraction by the benzylic terminus than to that for the alkyl terminus of biradical 2. All spectra observed show a similar E/A polarization pattern. The experimental spectrum of radical (6PD) obtained on the photolysis of ketone (5PD) and the simulated spectrum are shown in Figure 3. The presence of a tert-butyl substituent in the para position of the phenyl ring simplifies the analysis of the spectrum. The major quartet feature of the spectrum shows that the splittings due to α and β hydrogens are identical within the accuracy of the measurement. The triplet of triplets feature of the spectrum readily allows computation of the values of the HFC constants for ortho and meta hydrogens. The HFC constants evaluated are summarized in Table I.

For the radical (6ME) with a p-methyl substituent in the phenyl ring, the HFC pattern is more complicated (Figure 4a), but nevertheless its simulation is unambiguous (Figure 4b) and yields accurate values of hyperfine splittings. Despite the high spectral resolution achieved, the splittings of α and β hydrogen atoms cannot be distinguished. The same is true for the two nonequivalent ortho protons (vide infra).

The ESR spectra of radicals (4) and (6SU), produced by scavenging of biradicals generated in the photolysis of 3 and 5SU, coincide experimentally as expected, since they differ only in the number of methylene groups in long alkyl chain. The spectrum of radical (4) is shown in Figure 5 together with its simulation. A more complicated hyperfine pattern was observed for radical 6SU. This feature prevents an accurate evaluation of HFC constants for ring hydrogens, but the splittings of α and β hydrogens could still be determined with reasonable accuracy (Table I).

When all ring hydrogens are substituted by D atoms (radical 6PD) the structure of the ESR spectrum collapses into four
The splittings evaluated in Table I show that while the splittings of ring are in the order of the four other radicals. This feature is readily observable in the inset of the experimental spectrum (Figure 6a) or benzene. Its simulation (Figure 6b) shows the absence of the apparent doublets indicated with arrows.

An interesting issue involves the comparison of the HFC constants obtained for scavenging of biradicals with those for smaller structurally similar monoradicals. As far as we know, HFCs of 1-phenylalkyl radicals have been reported for the simplest members, i.e., the benzyl and 1-phenylethyl radicals. For longer alkyl chains the splittings of the two ortho protons can vary somewhat from those of the simpler monoradicals. A well-resolved spectrum of radical 10 is observed when ketone 9 is photolyzed in triacetin (Figure 7a) or benzene. Its simulation (Figure 7b) reveals that the two ortho protons are not equivalent since their splittings are distinctively different. This feature is readily observable in the inset of Figure 7, where the apparent doublets are indicated with arrows.

The activation energies and preexponential factors of this systematic study of the influence of different substituents upon the HFCs of substituted benzyl radicals reported in the literature.15-37 The presence of a methyl or tert-butyl group in the para position leads to higher delocalization of the unpaired electron away from the benzyl position and causes extra stabilization of the benzyl radical. The delocalization leads to a decrease in the benzyl delocalization and thus to a decrease in the benzyl hyperfine splittings, since both are proportional to its value.
TABLE II: Absolute Values of HFC Constants of Several Small Substituted Benzylic Radicals

<table>
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<th>A&lt;sub&gt;1&lt;/sub&gt;</th>
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<td>benzene, rt</td>
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- This work. The uncertainty for all splittings measured is ±0.05 G.

A comparison of Tables I and II shows that, although the hyperfine splittings for the two series are similar, they do not match exactly, especially for the β-hydrogens. This is not surprising since the splittings of β hydrogens are caused by hyperconjugation and depend considerably upon the angle between the orbital of the unpaired electron and the C-H bond. Increasing the bulk of the alkyl substituent in the α position alters its steric interaction with the benzylic fragment and diminishes the splittings of β hydrogens (Tables I and II). Therefore, because of these conformational effects, which may be subtle, small benzylic monoradicals may not serve as accurate models for the corresponding radical sites in biradicals. Thus, while the ESR spectra of small radicals usually show much better spectral resolution, the proposed approach based on the scavenging of one of the biradical termini provides a direct way to measure the HFC constants of the other with a high accuracy and with a local molecular conformational structure that is expected to be very similar to that of the biradical. We note, however, that this approach is based on the assumption that electron spin interactions have no influence on the HFC constants. We are unaware of any reason to expect such influence in the systems investigated.

Conclusions

The hyperfine splittings of one biradical terminus can be measured directly if the other terminus is scavenged with an appropriate spin trap. To be amenable to experimental investigation, such a measurement requires a selective scavenging of one of the biradical termini. BrCCl<sub>3</sub> is a selective scavenger of the acyl terminus of the biradicals produced by photolysis of a variety of cyclic ketones. Thus, transformation of the acyl—benzyl biradical into a substituted benzylic monoradical by photolyzing cyclic ketones in the presence of BrCCl<sub>3</sub> (Scheme I) allows the ready evaluation of the HFC constants of benzylic biradical termini. This procedure allows the evaluation of the HFC constants of excellent monoradical models of one of the biradical termini under the same experimental conditions as those employed for detection of biradical ESR spectra and does not require chemical synthesis of monoradical analog precursors. Splittings of several benzylic radicals were measured. Splittings of β hydrogens are clearly smaller for longer alkyl chains than for the simpler systems and presumably are the result of different steric restrictions. At the same time, all the spectra detected are in agreement with Scheme I. This lends further support for the assumption that the acyl moiety of the biradical efficiently abstracts Br atom from BrCCl<sub>3</sub> and that the latter is a good scavenger of acyl-containing biradicals. The method is also effective for the selective scavenging of the acyl moiety of biradicals produced from α,α′-polymethylated cyclic ketones.

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References and Notes