Table I. Incorporation of Chirally Tritiated Octanoate into Lipoate

expt	preCursor	³ H/ ¹⁴ C for precursor	³ H/ ¹⁴ C for lipoate	% ³ H retention
1	$[6(S)-6-^{3}H-1-^{14}C]-2$	4.13	3.47	84
2	$[6(R)-6-^{3}H-1-^{14}C]-2$	4.40	0.48	10

adduct of (+)- α -pinene (81% optical purity) and 9-BBN yielded the S alcohol 11 whose optical purity was presumed to be ~80%. Reduction of 10 with the adduct of (-)- α -pinene (optical purity 74%) generated the R alcohol 12 with an optical purity presumed to be \sim 72%. The two chirally tritiated alcohols 11 and 12 were converted to their tosylates and the latter compounds treated with lithium diethylcopper.² Since the reaction of dialkylcuprates with tosylates proceeds with inversion of configuration at the sulfonate bearing carbon atom,¹² this reaction sequence transforms the S alcohol 11 into the S acetal 13 and the R alcohol 12 into the R acetal 14.¹³ Ozonolysis of the chirally tritiated acetals and base-catalyzed hydrolysis of the resulting ethylene glycol esters² then produced sodium $[(6S)-6-^{3}H]$ - and $[(6R)-6-^{3}H]$ octanoate (15 and 16, respectively). The two samples of chirally tritiated sodium octanoate were each mixed with sodium [1-14C] octanoate and the tritium to carbon-14 ratios of each doubly labeled mixture were determined in the manner previously described.² The two doubly labeled precursors were then administered to shake cultures of E. coli and the lipoic acid isolated as the $S_{1}S'$ bis(p-phenylbenzyl) derivative.² The derivative from each experiment was recrystallized, converted to its methyl ester, chromatographed, and then recrystallized to constant specific radioactivity and constant tritium to carbon-14 ratio. The results of these experiments are summarized in Table I.

The tritium to carbon-14 ratios of the lipoic acid derivatives isolated in these experiments clearly demonstrate that sulfur is introduced at C-6 of octanoic acid with loss of the 6-pro Rhydrogen atom. Since the absolute configuration of lipoic acid at C-6 is known to be R,¹⁴ it follows that sulfur is introduced at C-6 of octanoic acid with inversion of configuration at that prochiral center. This observation suggests that the mechanism of sulfur introduction involves a multistep process. An obvious possibility which would account for the observed stereochemistry is hydroxylation at C-6 of octanoate with retention of configuration,15 activation of the hydroxyl group, and displacement of the activated group by a sulfur nucleophile. In view of the apparent similarity between the modes of sulfur introduction in the biosynthesis of lipoic acid² and biotin,³ one would predict that the introduction of sulfur at C-4 of dethiobiotin should also proceed with inversion of configuration. Experiments designed to test this prediction are in progress.

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Time-Resolved Electron Paramagnetic Resonance and Flow Fourier Transform Nuclear Magnetic Resonance Study in Radiation Chemistry. An Example of Overhauser CIDNP¹

Sir:

Parallel study of CIDEP and CIDNP^{2a-c} in radiation chemistry^{2d} has allowed observation of a straightforward example of polarization transfer between electron and nuclear spin systems by electron-nuclear cross relaxation. While this Overhauser CIDNP can be observed in many related systems, we will discuss the aqueous acetate radiolysis, since we have made extensive study of both CIDEP and CIDNP in this system.

The experiment is schematically outlined as follows:

$$e_{aq} \xrightarrow{[e_{aq}]{\cdot R]}} e_{aq} \xrightarrow{[(\downarrow)]{}} \xrightarrow{CICH_2CO_2^{-}} \cdot CH_2CO_2^{-}(\downarrow)$$

$$CIDEP \qquad CIDEP$$

$$\rightarrow (CH_2CO_2^{-})_2(\downarrow) \quad (1)$$

$$CIDNP$$

The hydrated electron is one of the primary radicals in aqueous radiolysis.^{2d} Dissociative electron capture by haloacetates yields the acetate radical; in turn, this radical can undergo bimolecular reaction yielding succinate.

The hydrated electron can be prepared with its electron spin polarization in emission (\downarrow) as shown by the CIDEP observed using time-resolved EPR. The electron spin polarization is transferred to the acetate radical (\downarrow) (CIDEP observed by time-resolved EPR) and subsequently the nuclear spin of the (diamagnetic) product succinate can be observed in emission (\downarrow) as well (CIDNP using flow FT NMR). We will discuss each of these steps in turn.

Emission in e_{aq}^{-} . Fessenden has observed that several radicals (from carbonate (CO₃⁻), phosphite (\cdot PO₃²⁻), phenol (phenoxyl), etc.) yield emissive CIDEP in e_{aq} ^{-.3} Since the electron g factor is the smallest of all these radicals, this unusual polarization has been rationalized by proposing that the radical pair $\overline{e_{aq}} \cdot R$ (where R is one of the aforementioned radicals) reacts into the triplet state of the products. (This amounts to an "inverse" g-factor effect.) This somewhat unusual mechanism of radical-pair CIDEP has yet to be substantiated. Our recent CIDNP studies in these systems have provided further indications that a g-factor effect is involved in reactions of e_{aq}^{-} with the CO₃⁻ and phenoxy radicals.⁷



Figure 1. CIDEP spectra from 0.2 M sodium chloroacetate (pH ~13, 2- μ s delay, $a_{\rm H} = 21.2$ G, He): upper, "normal" S-T₀ CIDEP; lower, CIDEP with shift to emission observed when solution contains 0.5 M sodium hypophosphite. (Quartz transient deleted.)

However, the field dependence of CIDNP in succinate, acetate, and other systems⁷ implicates an S-T₋₁ polarization mechanism in e_{aq} reaction with the phosphorus-centered radicals $(a_p > 400 \text{ G})$.

Irrespective of mechanism, for our purposes here it is important that by using such radicals we can prepare e_{aq}^{-} in an emissive electron spin state.

CIDEP in the Acetate Radical. Our submicrosecond timeresolved EPR studies have shown that, when the hydrated electron reacts with chloroacetate, it transfers its spin population to the resulting radical.4 (This has also been observed by Verma and Fessenden.⁵) The time-resolved EPR spectrum of the acetate radical, obtained when e_{aq}^{-} is not polarized (Figure 1, upper), shows that e_{aq}^{-} simply transfers its equalized spin state population to the $\cdot CH_2CO_2^{-}$ radical and the "normal" S-T₀ CIDEP is observed.⁴ The low-field line is in emission, the center line is not polarized, and the high-field line is in enhanced absorption. When e_{aq}^{-} is prepared in emission (by generation in solutions containing phosphite, hypophosphite, carbonate, etc), ·CH₂CO₂⁻ CIDEP reflects this emission (Figure 1, lower). Now the CIDEP spectrum shows an overall shift to emission: the low-field emissive line is now more intense than the high-field enhanced absorption line, and the center line is now in emission as well. Clearly e_{aq} reacts with the substrate at least an order of magnitude faster than it relaxes $(e_{aq}^{-} T_1 \simeq 2-4 \ \mu s).^5$

CIDNP in Succinate. We have described previously how NMR CIDNP experiments are carried out in radiation chemistry.⁶ Briefly, we use a flow system that transfers solution from an irradiation cell in an external magnet (0-8 kG) to the spinning 5-mm tube in the NMR magnet (Bruker WP-80 FT NMR). Radical concentrations in our experiments are such that all chemistry is over in several microseconds and only the polarized products flow into the NMR probe. Our arrangement is well suited for routine variable field (0-8 kG) CIDNP study.

In a typical CIDNP study of acetate radiolysis, at high field we observe succinate in enhanced absorption (Figure 2, upper).⁸ In contrast, when e_{aq}^{-} is emissively polarized (vide infra), we observe succinate in intense emission at a 3500-G field paralleling that of the X-band EPR field (Figure 2, lower). The transfer of the electron polarization to the nuclear polarization occurs by (dipolar) cross relaxation in the acetate



Figure 2. CIDNP spectra from 0.2 M sodium chloroacetate (pH \sim 13, 3500-G field, He): upper, CIDNP observed when solution contains 0.4 M sodium sulfite; lower, CIDNP observed when solution contains 0.4 M sodium carbonate. Assignments: A, HOD; B, chloroacetate; C, succinate; D, acetate.

radical. As long as the radical lifetime is not longer than the nuclear T_1 in these radicals ($T_1 \simeq 10^{-5}$ s), this applies, and in our experiments the acetate radical half-life is typically in the range of 2–20 μ s.

In these experiments (with irradiation fields \sim 3500 G) nearly optimal conditions exist for polarization transfer from electron to nuclear spins, since electron-nuclear relaxation transition rates are comparable to the bimolecular reaction rate and the electron T_{1} .⁹

The Overhauser CIDNP effect has received much attention since it was the basis for the first explanation of the CIDNP phenomenon.¹⁰ Over the years there has been much speculation as to whether Overhauser CIDNP contributes to CIDNP in some systems.¹¹⁻¹³ The studied systems to date involve transfer of "triplet" electron polarization in photolysis. Quinone systems have been studied in detail by Adrian and Wan.⁹ Roth and coworkers have studied fluorine-substituted aryl alkyl ketones.¹⁴

In the pulse radiolysis experiments outlined above we believe to have a most clear-cut example of electron-nuclear polarization transfer. As we have found in all our CIDEP and CIDNP studies of radiation chemistry, the radical pair model is the dominant polarization mechanism. Overhauser CIDNP can be seen only in those products where the usual (RP) polarization routes are weak or nonexistent. Our ability to control both the magnetic field of reaction and the radical concentration makes this an ideal approach for the study of these phenomena. Furthermore, as the acetate system has been examined in the time domain 100 ns to ~50 μ s by EPR^{3,4} and variable-field flow NMR,⁶ no other chemical system has been so thoroughly examined by both CIDEP and CIDNP methods.

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Unambiguous Generation and Trapping of a Silabenzene

Sir:

Recently we reported the results of a reaction which appeared to involve generation and trapping of a long-awaited silabenzene.¹ Thus, when 1-chloro-1-methyl-1-silacyclohexadiene (1) was reacted with N-lithiohexamethyldisilazane in the presence of excess perfluoro-2-butyne, silabarralene 2 was obtained in 28% yield. While all of the results of that study



were totally consistent with the intermediacy of 1-methyl-1silacyclohexa-1,3,5-triene (3), we could not totally rule out a mechanism involving carbanionic attack by an initially formed pentadienyl anion followed by intramolecular displacement of chloride. Thus, we have sought a less ambiguous route to silabenzenes and will report here such a route.

The elegant synthesis of silacyclobutenes recently reported by Block² suggested a simple route to silabenzene 3. Block found that vacuum flow pyrolysis of, for example, diallylsilane 4 produced silete 6 in 41% yield. The reasonable mechanism suggested was a retro-ene reaction of 4 to generate silabuta-



diene 5, which in turn closes to the silacyclobutene.

Recognizing that an allylsilacyclohexadiene might possibly behave in the same fashion, we prepared 1-methyl-1-allyl-Isilacyclohexa-2,4-diene (7) from the reaction of chlorosilane 1^3 and allylmagnesium chloride in THF. Pyrolysis of 7 was conducted in a vertical quartz tube packed with quartz chips heated to 428 °C in a tube furnace. Acetylene (20 mL/min) was used both as reactant and carrier gas to produce a product mixture containing unreacted 7 (48%) and adduct 8, 1methyl-1-silabicyclo[2.2.2]octatriene, in 33.6% yield based on reacted 7.4



Adduct 8 was identified from its 100-MHz ¹H NMR spectrum ((DCCl₃) δ 0.81 (s, 3 H, SiMe), 5.15 (q of q, 1 H_A, $J_{AB} = 1.6 \text{ Hz}, J_{AC} = 7 \text{ Hz}, h\nu \text{ at } 6.57 \text{ collapses to q}), 6.57 \text{ (d}$ of d, 3 H_B , $J_{BC} = 11 Hz$, hv at 5.15 collapses to d), 7.41 (d of d, 3 H_C, $h\nu$ at 5.15 collapses to d)) and its high resolution mass spectrum which showed a molecular ion peak at m/e 134.0547 (15% calcd for C₈H₁₀Si 134.0552) with prominent ions at 119 $(100\%, M^+ - CH_3)$ and 93 $(35\%, M^+ - CH_3 - CH_3)$ HC=CH).

In a like manner copyrolysis of 7 and perfluoro-2-butyne (20 mL/min) at 450 °C afforded adduct 2 (~20%), which was



identical in all respects with 2 synthesized via dehydrochlorination of 1.1

This latter observation not only further demonstrates the utility of this method of silabenzene synthesis, but also strengthens our earlier claim that formation of 2 from the base-induced dehydrochlorination of 1 in the presence of perfluoro-2-butyne is evidence for the production of silabenzene 3 in that reaction.5

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 Compound 1 is conveniently prepared from the reaction of methylchlorosilylene and cyclopentadiene.¹ Triene 7 must be purified by GC and the
- yield, 61.4%, thus represents a minimum. This is a calibrated GC yield of 8 which was prepared at 150 °C on a 27-ft, (4)15% SE-30 on Chromsorb W column. Propene was identified in the product mixture by GC-MS.
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