solutions, the large magnetic field effect on the ^{13}C enrichment, and the specificity of enrichment at the carbonyl carbon?

The magnitude of the magnetic isotope effect may be computed from the expression P (the probability for formation of DBK from any radical pair), which is available from the theory of CIDNP:[2,3]

$$P \sim \epsilon \int_0^\infty F(t)|C(t)|^2 dt \qquad (2)$$

ϵ is the probability that ${}^1\overline{\mathrm{D}}$ pairs yield DBK, $f(t)$ represents the distribution of lifetimes among radical pairs, and $|C(t)|^2$ is the probability that by time t the radical pair will be in a singlet state. The product $f(t)|C(t)|^2dt$ may be viewed as the probability that a radical pair formed at $t = 0$ will form ${}^1\overline{\mathrm{D}}$ at time t.

CIDNP studies of the photolysis of DBK[10] are consistent with the idea that HFC provides an important mechanism for intersystem crossing in ${}^3\overline{\mathrm{D}}$. The most significant HFC in ^{3}D should be due to the coupling of the odd electron of $\mathrm{PhCH_2\dot{C}O}$ to a ^{13}C nucleus ($a \sim 130$ G).[11] Therefore, if ^{13}C HFC operates to control the rate of ISC of ${}^3\overline{\mathrm{D}}$ to ${}^1\overline{\mathrm{D}}$, and if ^{3}D pairs possessing no ^{13}C HFC are scavenged or decarbonylate at a rate faster than they convert to ${}^1\overline{\mathrm{D}}$, as photolysis proceeds $\mathrm{PhCH_2COCH_2Ph}$ *must become enriched in ^{13}C and the enrichment must occur predominantly at the carbonyl carbon*.

The photolysis of DBK in soap solutions produces radical pairs in micelles.[12] The explicit form of $f(t)$ in eq 2 for a radical pair in a micelle favors ^{13}C enrichment (relative to a homogeneous fluid solution) via two factors: (1) the "restricted dimensionality" for diffusional excursions[13] of a radical pair in the micelle[14] and (2) the high local viscosity[15] of the interior of a micelle. In effect, both of these factors should favor the efficiency of ${}^3\overline{\mathrm{D}} \rightarrow {}^1\overline{\mathrm{D}}$ interconversions by "slowing down" the ${}^3\overline{\mathrm{D}} \rightarrow$ FR processes. Further evidence that HFC is operating as the dominant mechanism for ^{13}C enrichment is found in the observation that the single-stage enrichment drops from 0.47 in the earth's magnetic field (~0.5 G) to 0.12 in the presence of a strong laboratory magnetic field (~15 000 G).

The mechanics of a HFC induced magnetic isotope separation are shown in Figure 2 in terms of energy surfaces. The crucial postulate is that HFC provides *a "hole"[16] on the "^{13}C triplet surface" which provides access to the DBK (S_0) surface and that no such hole exists on the "^{12}C triplet surface"*. A representative point that is put on the T surface (i.e., path a → b, eq 1) will follow a trajectory on the T surface which takes it to the "crucial geometries" required for ${}^3\overline{\mathrm{D}} \rightarrow {}^1\overline{\mathrm{D}}$ interconversion. The micelle enhances the probabilities of finding these geometries by providing a "reflecting boundary" for representative points that "overshoot" the hole. DBK, regenerated via path a → b → c → d → e *must* be enriched in ^{13}C, and incorporation of DBK into a micelle must enhance the process, the only question being the exact amount of the enrichment.

The idea of isotopic separation by employing HFC may be applied generally to any reaction involving a singlet-triplet crossing (or touching) along the reaction coordinate and possessing significant HFC at the structure corresponding to the crossing (or touching). Magnetic isotope effects may eventually be employed for the practical separation or enrichment of isotopes and the control of partitioning along reaction pathways involving intersystem crossing. In addition, they provide a novel mechanistic tool which complements CIDNP and which demonstrates the existence of diradicaloids and singlet-triplet crossings (or touchings) along a reaction coordinate.

Acknowledgment. The authors thank Professor W. R. Cherry for his assistance in the early stages of the experiment, Professor B. P. Dailey for use of his 15 000 G magnet, and Ms. Slavica Sporer and Mr. Iwao Miura for their expert assistance in obtaining quantitative mass spectra and NMR analysis. B.K. thanks the Schweizerischer Nationalfonds zur Foerderung der Wissenschaftlichen Forschung for their support. The authors especially thank Professor R. B. Bernstein for very informative discussions on isotope separations and for pointing out to us a useful format for expressing isotopic enrichment factors.

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Received August 13, 1978

A Phosphoranide[1] Anion—Direct Observation of a Tetracoordinated Phosphorane Species

Sir:

Although tetracoordinated tetrahedral phosphonium cations[2] and tetracoordinated trigonal-bipyramidal (TBP) phosphoranyl radicals[3] are well known, the anionic species derivable from the radicals by one-electron reduction, phosphoranide[1] anions, have received scant attention.[4] We here report the direct observation of such a species.

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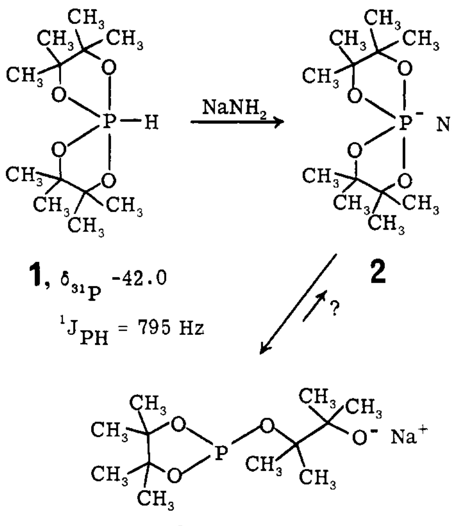


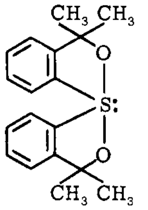
1, $\delta_{^{31}P}$ -42.0
$^1J_{PH}$ = 795 Hz

2

3, $\delta_{^{31}P}$ +140.0

Phosphoranide intermediates or transition states have been proposed for nucleophilic substitutions at tricoordinated phosphorus.[4,5] Deprotonation of **1** is postulated[4d] to lead to an equilibrium mixture of spirocyclic phosphoranide salt **2** and monocyclic phosphite alkoxide **3**, but spectroscopic evidence for the phosphoranide anion was not obtained. The ^{31}P NMR spectrum (+140.0 ppm) gave evidence more consistent with the open-chain tautomer **3**.[4d]

The earlier reported[6] synthesis of sodium phosphoranoxide **5** was undertaken, in part, as a test of the notion that structural features imparting unusual stability to the sulfurane oxide[7] which is isoelectronic with **5** would also render **5** observable. Sulfurane **4** has also been shown[8] to be very stable, suggesting to us the possibility, here confirmed, that the isoelectric phosphoranide anion of **6** might also be sufficiently stable to allow direct observation.



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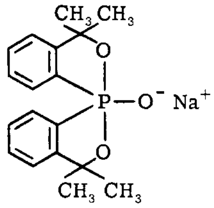

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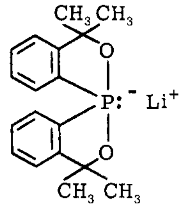


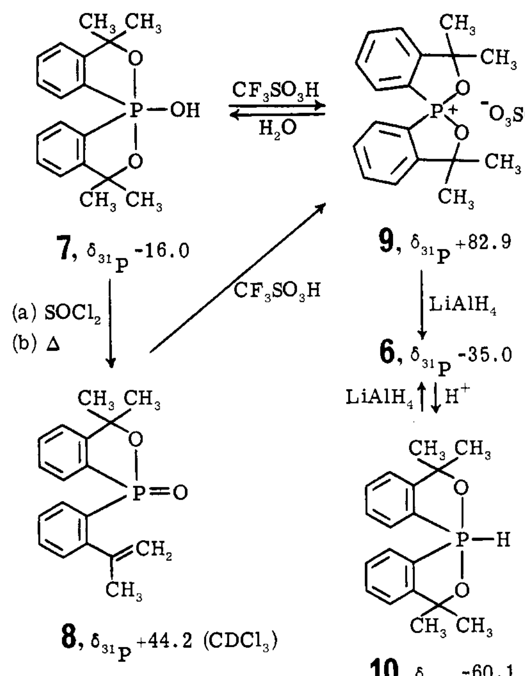
6

We have recently reported the isolation of a crystalline compound which, at least in some solvents, has structure **7**. Either **7** or its dehydration product **8** gives[9] phosphonium trifluoromethanesulfonate (triflate) (**9**), mp 153 °C, upon treatment with triflic acid in chloroform or dry methanol (Scheme I). The remarkably[10] stable triflate, **9**, is not hygroscopic, but it is easily hydrolyzed to **7** in moist chloroform.

Most interesting is the reduction of **9** by lithium aluminum hydride. Molecular hydrogen is evolved and ^{31}P NMR shows a new compound which has a typical phosphorane chemical shift (−35.0 ppm). Protonation of this phosphoranide gives the P-H phosphorane **10**, mp 99 °C (−60.1 ppm, $^1J_{HP}$ = 680 Hz). The phosphoranide **6** is also obtained from the reaction of **10** and LiAlH$_4$, suggesting that **10** is an intermediate in the reduction of **9** to **6**.[11]

The reaction of PCl$_3$ with the Grignard reagent prepared from 2-(2-bromophenyl)-2-propanol[6] gives, among other products, a magnesium phosphoranide which upon acidification gives **10**.

Scheme I



7, $\delta_{^{31}P}$ -16.0

9, $\delta_{^{31}P}$ +82.9

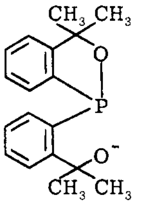
6, $\delta_{^{31}P}$ -35.0

8, $\delta_{^{31}P}$ +44.2 (CDCl$_3$)

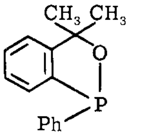
10, $\delta_{^{31}P}$ -60.1

The bidentate ligands used to form the compounds reported here have one electropositive (C) and one electronegative (O) center for coordination to phosphorus to form five-membered rings. The usual "five-membered ring effect"[12] is enhanced in spirobicyclic derivatives of sulfur(IV)[12] or phosphorus(V)[6] with such ligands. The conformation with apical oxygen and equatorial carbon has a substitution pattern enhancing the difference in electronegativity between the central atom and the apical atoms in the three-center bond, a factor thought[13] to favor such symmetrical four-electron bonds. In this connection it is interesting to note that neither type of hypothetical symmetrically substituted spirophosphoranide, with four oxygen[4d] or four carbon[4c] ligands, appears to be as stable as the one reported here with two oxygen and two carbon ligands.

Alkoxide phosphinite **11**, the open-chain tautomeric alternative structure for **6**, is ruled out by the difference in ^{31}P chemical shift for this compound (−35.0 ppm) and model phosphinite **12** (+113.0 ppm).[14,15]



11



12, $\delta_{^{31}P}$ + 113.0 (CDCl$_3$)

The ^{31}P NMR chemical shift for P-H phosphorane **10** (−60.1 ppm), 25.1 ppm to higher field than that for its conjugate base, phosphoranide **6**, suggests a greater dependence on coordination number than on negative charge. The same sort of upfield shift is seen upon protonation of diphenyl phosphide to yield the phosphine.[16]

Acknowledgment. This research was supported in part by a grant to J. C. M. from the National Cancer Institute (HEW PHS CA 13963).

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(15) Two additional lines of evidence can be cited favoring the closed-ring tautomeric structures **6** and **10**. Benzylation of **6** with excess benzyl bromide occurs only at P to give a phosphorane. It is perhaps even more significant that 30% hydrogen peroxide fails to oxidize **10** under a variety of conditions which lead to oxidation of phosphorus(III) compounds which are models for the open-chain tautomer of **10**, the conjugate acid of **11.**

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(17) On leave from Israel Institute for Biological Research, Ness Ziona, Israel.

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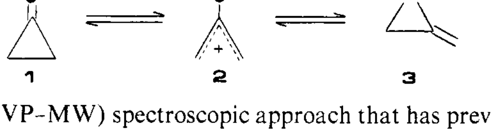
Allene Episulfide[1]

Sir:

In view of the fascinating chemistry associated with the cyclopropanone–allene oxide tautomeric system,[2] we have initiated an investigation of the analogous, little studied, cyclopropanethione–allene episulfide system (eq 1).[3] Anticipating that the parent compounds **1** and **3** would be highly reactive we have employed a flash vacuum pyrolysis–microwave (FVP-MW) spectroscopic approach that has previously proven successful in the characterization of other reactive organosulfur molecules.[4] We report herein the generation and microwave structure of allene episulfide (methylenethiirane, **3**). We also provide data relevant to the processes depicted in eq 1.



(1)

Compounds **4**[5] and **5** (prepared in 54% yield from 5-norbornenone using the lithio-2-(methylthio)-2-oxazoline reagent[6,7] (**6**)) seemed likely thermal precursors of **1** and **3**, respectively.[8] However, using the FVP-MW procedure we find that both **4** and **5** cleanly decompose to allene episulfide (**3**) at pyrolysis temperatures of 600–700 °C, with no detectable amounts of cyclopropanethione being formed.[9] Pyrolysis of **5** ^{13}C or d_2 labeled on the thiirane ring[10] afforded allene episulfide with labeling equally distributed (±5%) between the ring and exocyclic methylene groups (C_2 and C_3 in Figure 1), as indicated by microwave analysis. These observations are consistent with the mechanistic picture presented in eq 2 in which it is suggested that the ^{13}C and deuterium scrambling in allene episulfide (**3**), the formation of **3** from cyclopropanethione trimer **4**, and the formation of ethylene in both of these pyrolyses proceed by way of a thioxyallyl ion (**2**) (or a related diradical resonance structure) as a common intermediate.[11,13] We further interpret these results to indicate that allene episulfide is thermodynamically *more stable* than cyclopropanethione, in apparent contrast to the order of stability in the allene oxide–cyclopropanone system.[2,14]

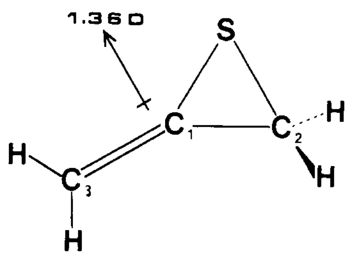
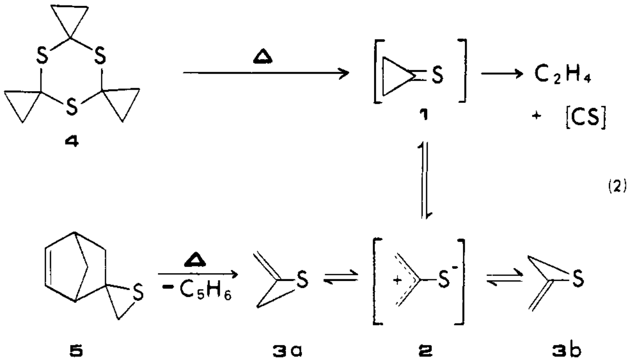
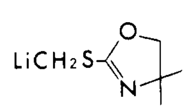


Figure 1.



(2)

Allene episulfide is also formed on pyrolysis (520 °C) of anthracene adduct **7**[16] and on heating tosylhydrazide salt **8**.[3b,18] Efforts to generate C_3H_4S isomers **1** or **3** by pyrolysis of cyclopropyl precursors of type **9a–c**[19] lead instead to the formation of another C_3H_4S isomer, identified by its microwave spectrum as thioacrolein.[21] We postulate that this latter compound arises from a ring-opening process such as that depicted in eq 3.



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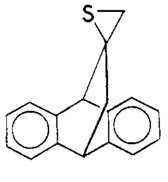
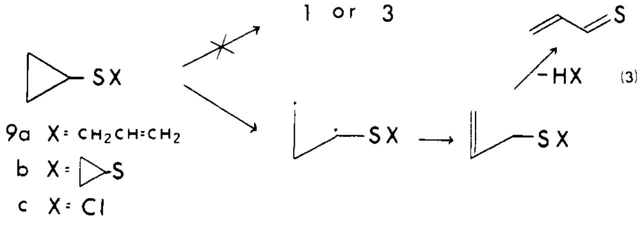


7

8



(3)

The identity of allene episulfide (**3**) has been established unambiguously by a microwave substitution structure determination. Spectral assignments of the normal isotopic species, along with the four ^{34}S and ^{13}C singly-substituted species and

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