(15) Labeling experiments are underway to test for this possibility.

(16) Carbon peak (δ 152.8) half-width = 25.8 Hz at $-130\,^{\circ}$C and assuming a separation of 300 ppm for the two carbons in a conventional secondary cation two-site NMR exchange.

(17) The existence of these bridged cations may be related to the favorable energy release involved in forming a decalin-type geometry from the strained cyclodecyl system. However, we believe that the "extra" electronic stabilization of a symmetrical bridged species creates an even more stable conformation.

(18) Up to $-117\,^{\circ}$C, there is no substantial further line broadening in either the 2 H low-field peak or the 1 H high-field peak, $k_{exchange} \leqslant 50\ sec^{-1}$, $\Delta G^{\ddagger} \geqslant 8$ kcal/mol for a possible 1,2-H shift, based on simulated line-broadening curves calculated for this exchange.

(19) For example, in the cyclopentyl cation, these shifts are so fast that only one carbon and one proton peak is observed, even at the lowest temperatures.[20]

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(23) The term "hydride shift" in carbocation rearrangements has in the past been informally criticized on the grounds that the overall charge would likely be "smeared out" between the two carbons involved and the migrating hydrogen, i.e.

$$\ce{>C-H + ^+C<} \longrightarrow \left[\ce{>C---H---C<}\right] \longrightarrow$$
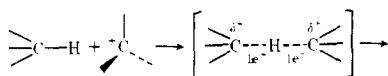
and hence that the term is useful only in an electron-bookkeeping sense. However, if our postulated bridged cations are any indication, the migrating hydrogen is indeed "hydride-like" at the midpoint of the transfer. These bridged cations emphasize the stability associated with charge alternation, i.e. + − +. The higher field position of the bridging hydrogen in the secondary ion, compared with **2**, suggests that more positive charge on carbon simply reinforces more negative charge on hydrogen.

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Received June 23, 1978

"Tailored Detection" of Nuclear Magnetic Resonance Signals: Application to the Assignment of Carbon-13 Spectra

Sir:

We propose a new method for treating data in a Fourier transform NMR experiment in order to select signals which appear at certain predetermined frequencies and calculate their contribution to the total signal intensity. The technique might be used to determine the relative proportions of two components in a mixture, for monitoring the growth and decay of transient intermediates, or for comparing an unknown experimental spectrum with a library of stored spectra. It will also be shown to be useful for reducing the noise content of projections of two-dimensional Fourier transform spectra.[1-3] Several authors have described NMR experiments where the *excitation* is frequency selective or "tailored" to a particular requirement;[4-6] the present method uses an equivalent "tailored detection" scheme.

To illustrate the principle, consider the problem of making a quantitative comparison between an experimental spectrum and a reference spectrum, as in the example of a library search of NMR data to match an unknown spectrum. This may be achieved by multiplying the experimental free induction decay $E(t)$ with that of the reference $A(t)$ and integrating the product. The result is a measure of the overlap between the experimental and the reference spectrum. The idea may be extended to the multiplication of $E(t)$ with an *artificial* time-domain reference signal $A'(t)$, obtained by Fourier transformation and suitable weighting of a "stick spectrum" defined by the operator.[7] The Fourier transform of $A'(t)$ resembles this stick spectrum but has finite line widths determined by the weighting function. It may be thought of as a "mask" $A'(f)$ constructed to pass certain frequency compo-
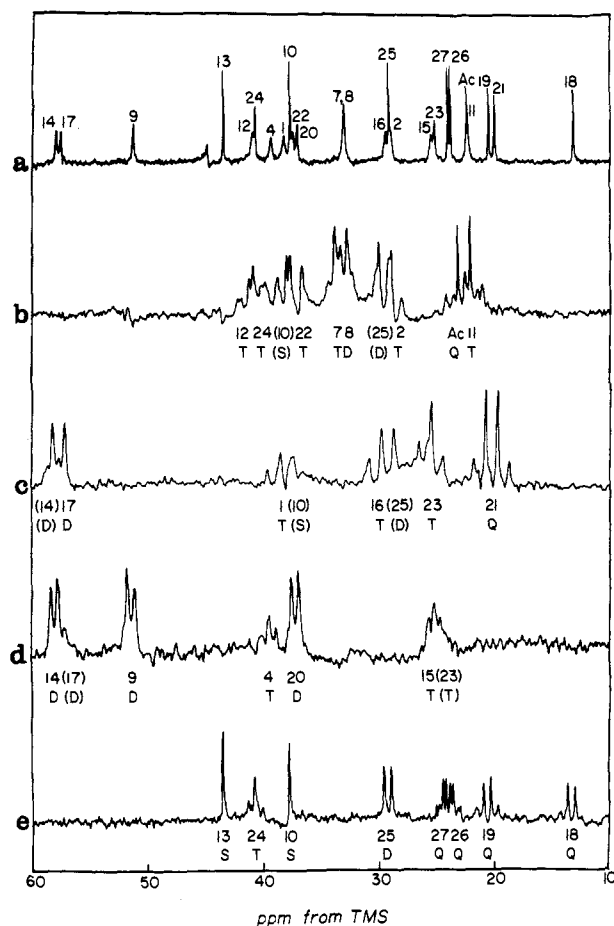
nents of the spectrum $E(f)$, the Fourier transform of $E(t)$. The line widths of $A'(f)$ and $E(f)$ may be matched in order to optimize signal-to-noise ratio. Multiplication and integration of time domain signals has the twin advantages of speed (since the NMR signal may be processed as it is acquired) and economy of data storage (since the incoming free induction signal need not be stored). An "on-line" masking process necessarily leads to a loss of information; in some applications it might be preferable to store the entire experimental free induction signal and then later use suitable masks to extract various special types of information off-line.

We concentrate on a particular application—the improvement of signal-to-noise ratio in an experiment which presents ^{13}C NMR spectra in a form where all proton–carbon splittings are scaled down by a suitable constant factor R. This "J-scaling" experiment[8] can considerably reduce the confusion caused by overlapping multiplets in conventional coupled ^{13}C spectra, and avoids some of the instrumental problems of off-resonance decoupling.[9] The pulse sequence is described in detail elsewhere.[8] The principle is to establish an evolution period t_1 during which proton-coupled carbon-13 precession takes place for a fraction $1/R$ of the time, broad band decoupling being used for the remainder of t_1. A series of measurements of the NMR response is made over a range of values of t_1, building up an "interferogram" $S(t_1)$. If the final J-scaled spectrum is to contain N significant points, then N separate measurements are needed to construct $S(t_1)$, a time-consuming operation which leads to poor sensitivity. The original version of the J-scaling experiment[8] employed a refocussing method to improve the signal-to-noise ratio, but this

Figure 1. The ^{13}C NMR spectrum of the aliphatic region of cholesteryl acetate: (a) noise decoupled; (b–e) with selected resonances showing scaled-down proton–carbon splitting. The breakthrough of signals from nearby nonselected resonances is indicated by parentheses.

suffered practical difficulties with analogue filtration. The tailored detection method is a simpler and more effective way of regaining the lost sensitivity, since it may be set up to act as a matched digital filter for the designated frequency components. The requisite mask is made up to match selected lines in the noise decoupled spectrum and each incoming free induction decay $E(t)$ is multiplied by the corresponding time domain reference $A'(t)$, and the integral $\int E(t)A'(t)dt$ stored as one point on the interferogram $S(t_1)$. Fourier transformation of $S(t_1)$ generates a J-scaled spectrum with optimum sensitivity. This is because a J-scaled spectrum is equivalent to a skew projection of a two-dimensional spectrum,[10,11] the process of tailored detection corresponding to projection of selected traces (those carrying the signals), intermediate noisy traces being suppressed.

Cholesteryl acetate provides an example of a reasonably complicated carbon-13 spectrum to illustrate the adaptation of tailored detection to the J-scaling technique. Spectra were obtained on a Varian CFT-20 spectrometer modified as described earlier.[8] Figure 1a shows the broad band decoupled spectrum of the aliphatic region, comprising 25 resonances, several of which fall in crowded groups of nearly degenerate frequencies.[12] Lines in the noise decoupled spectrum are selected for the masks $A'(f)$ in such a way to avoid confusing overlap of mutliplets in the J-scaled spectrum. For the case of cholesteryl acetate, four separate mask spectra were used, each with line broadening chosen to match the experimental line widths, and each concentrating as far as possible on well-separated chemical shifts. Careful choice of the scaling factor helps clarify the resulting J-scaled spectra; traces b and c of Figure 1 used a scaling factor of $R = 6$ while d and e used $R = 10$. Several near degeneracies in chemical shifts make the assignment quite challenging. For example in Figure 1b, the experiment designed to pick out the response of site 22 (a triplet) cannot avoid some breakthrough of the sharp singlet resonance from site 10, and similarly the triplet from site 2 has a superimposed sharp doublet from site 25. However, even lines that are unresolved in the decoupled spectrum may be assigned if they have different multiplicities, for example the quartet from the acetate methyl group and the triplet from site 11 in Figure 1b.

Several types of NMR experiments involve monitoring the peak of a chosen resonance as a function of time; the examples include spin-lattice relaxation measurements, the study of transient intermediates or transient polarization effects, and the determination of chemical exchange rates by following magnetization transfer. By acting as a matched filter and calculating an integral, tailored detection gives a much better measure of intensity, less susceptible to noise and variations of instrument resolution; it can also operate on several lines at once. Applied to double Fourier transform experiments, this procedure should prove generally useful in optimizing the signal-to-noise ratio of projections and cross sections of two-dimensional spectra. As has been demonstrated, the method is also valuable in analogous one-dimensional experiments such as J scaling and J spectroscopy.[13]

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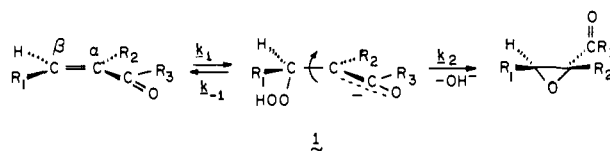
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Received June 5, 1978

Angle and Torsional Strains as Tools for Enhancing the Kinetic Stability of β-Hydroperoxy Ketones

Sir:

The alkaline peroxidation of enones, discovered by Weitz and Scheffer[1] and first kinetically scrutinized by Bunton and Minkoff,[2] has more recently been shown to be nonstereospecific but highly stereoselective in acyclic systems.[3-7] Irrespective of the geometry of the starting α,β-unsaturated ketone, the product having the less hindered carbonyl group is kinetically favored, a phenomenon attributed to overlap control.[7] These observations have implicated C_α-C_β rotational equilibration during the lifetime of the enolate anion **1** prior to ejection of hydroxide ion. Evidence has been presented to in-

dicate not only that the rate-determining step is k_1, the attack of HOO$^-$ on the β carbon,[2] but that reversal of hydroperoxide anion addition may compete with closure to the epoxy ketone $(k_{-1} > k_2)$.[7]

Greater appreciation of the above mechanism can be gained by considering several extreme possibilities. One of these is the condition where $k_2 \gg k_P$ such that protonation of **1** by solvent is not encountered. The lone established example of this behavior has been reported by Pappas and Bao who observed that the epoxidation of phenalenone (**2a**) with alkaline deuterium peroxide afforded **4a** with no deuterium incorporation.[8] In their hands, the reverse experiment with **2b** and HOO$^-$ gave only **4b**. Since the rate of proton transfer from water to an enolate anion has been estimated to be on the order of 10^5 s,[8,9] the rapid cyclization of **3** may be close to a limit for nucleophilic attack on a peroxide linkage.

2a, R = H   **3**   **4a**, R = H
b, R = D   **b**, R = D
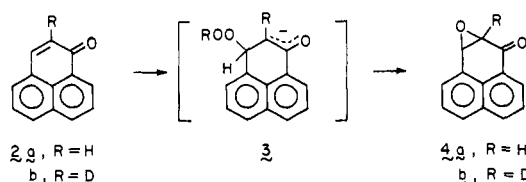
We now describe novel experimental findings that are at the other extreme of the scale, that is where the barriers associated with k_{-1} and k_2 have become so high that enolate **1** is relegated