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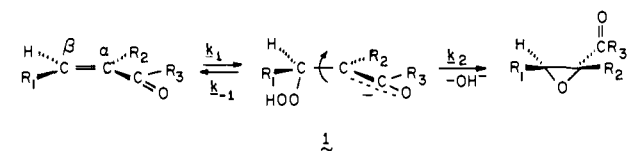
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Angle and Torsional Strains as Tools for Enhancing the Kinetic Stability of β-Hydroperoxy Ketones

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
b, R = D

3

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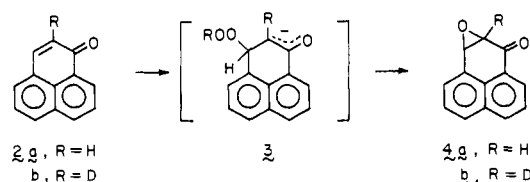
We now describe novel experimental findings that are at the other extreme of the scale, that is where the barriers associated with k_{-1} and k_2 have become so high that enolate **1** is relegated

5   6   7

8   9   10

a = saturated
b = unsaturated

16   17   18
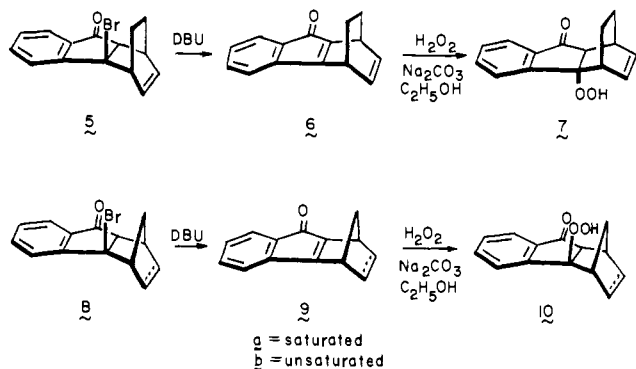
exclusively to protonation by solvent. Alkali stable β-hydroperoxy ketones, a class of compounds which seemingly has escaped prior isolation,[10-13] are thereby produced.

The pivotal indenones 6 and 9b were prepared by Diels–Alder cycloaddition of 3-bromoindenone[14] to 1,3-cyclohexadiene (C_6H_6, $BF_3\cdot Et_2O$, 5 °C, 2 h) and cyclopentadiene (CH_2Cl_2, 25 °C, 12 h), respectively, followed by dehydrobromination of the resulting 5 and 8b with an amidine base. Bromo ketone 8a, obtained either through sequential catalytic hydrogenation and benzylic bromination (NBS) of the simpler indenone adduct or preferably by reduction of 8b, served as the starting material for 9a. Whereas 6 and 9a proved to be entirely stable, 9b was found to be labile with respect to formation of a high melting (>225 °C) substance and was utilized immediately upon its generation.

The alkaline peroxidation of 6 at 25 °C led efficiently to hydroperoxide 7 (mp 123-124 °C; 69% after silica gel chromatography),[15] the stereochemical assignment of which is secured by its characteristic ^1H NMR spectrum and cyclization to 11 (mp 94-95 °C) when treated with 2,4,4,6-tetrabromocyclohexa-2,5-dienone.[16] The kinetic preference for endo


11   12a, R = H   13
       b, R = CH₃
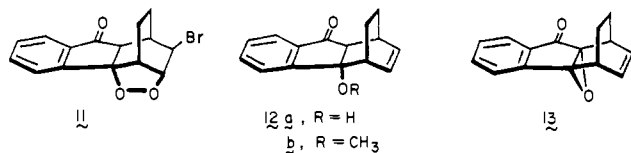
attack conforms to the lower heat of formation calculated for stereoisomer 7 relative to its exo counterpart.[17] Stannous chloride reduction of 7 afforded 12a which proved spectroscopically different from 5, but closely allied to 12b, the product of direct methanol addition to 6.

Entirely similar results were realized with 9a and 9b which furnished 10a (mp 124-125.5 °C, 60%) and 10b (unstable oil, 82%). These hydroperoxides were individually reduced to 14 and 15, and shown in turn to be stereochemically related through catalytic hydrogenation.

14   15
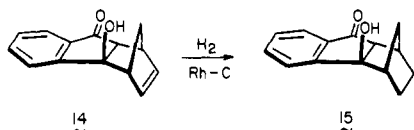
While submission of 7 to more alkaline conditions (15% aqueous NaOH, CH_3OH, 25 °C) did result in epoxy ketone formation (55% of 13 after 5 h), 10a and 10b proved totally unreactive toward base. Their inability to cyclize is not due to the kinetic nonacidity of the α-keto proton, for deuterium exchange experiments under less basic conditions (Na_2CO_3, CH_3OD, D_2O, 25 °C) led to isotopic exchange at both >CHCO- and -OOH, nor was reconversion of 10a and 10b to their precursor indenones observed in a variety of alkaline media.

As a test of the premise that angle and torsional strains actually control the kinetic properties of the intermediate enolate
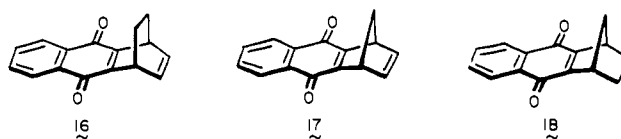
anions, the susceptibility of naphthoquinones 16-18[18] to alkaline peroxidation was also examined. Molecular models reveal that fusion of a six- rather than a five-membered Michael acceptor to a representative bicyclic framework results in a lessening of energetically unfavorable structural constraints during the incorporation of a three-membered epoxy ring across the central bond. In line with this a priori assessment, the epoxidations of 16-18 were found to proceed to completion during 45 min to 2 h at 25 °C (30% H_2O_2, Na_2CO_3, C_2H_5OH); only in the case of 17 was a trace of residual hydroperoxy ketone observable (TLC analysis). Of some interest is the stereoselectivity of these reactions. Whereas the product ratio in the case of 16 was 14:1 in favor of the endo isomer (O syn to the isolated double bond), that in norbornadienyl example 17 was more equitable, although reversed (1 part endo:3 parts exo). Quinone 18 gave rise exclusively to the exo epoxide.[19]

Accordingly, the dominant forces underlying the unprecedented behavior of 6, 9a, and 9b toward ⁻OOH appear to be angle and torsional strain.[20] The incipient formation of a three-membered ring which incorporates the C_2 and C_3 atoms of a norbornyl system generates eclipsing interactions which are significantly increased through added fusion of a five-membered ring. In the present instance, prevailing kinetic and steric factors guide the initial stereoselectivities of nucleophilic hydroperoxide attack.[21] For indenones 9a and 9b, bonding occurs preferentially syn to the methylene bridge. The resulting enolate anions can neither reverse the Michael process nor cyclize to the epoxy ketone. For the enolate anion of 7, the strain associated with ring closure is somewhat lessened owing to greater conformational flexibility and cyclization that can ultimately be achieved.

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(22) NATO Postdoctoral Fellow with financial support provided by the CNRS.

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α-Silyloxy and α-Hydroxy Manganese Alkyls. Generation via a New Five-Membered Metallocycle

Sir:

An ongoing research objective in our laboratory has been the generation of ligand types believed to be intermediate in the metal-catalyzed reduction of CO by H_2.[1-3] Since the ultimate reduction products range from methane and methanol to higher alkanes and alcohols (Fischer–Tropsch process),[4,5] there is considerable interest in discerning the factors which control product *selectivity*, and in developing milder and homogeneous catalysts for accomplishing these transformations.[6] Communicated herein are our initial efforts at preparing complexes containing the α-hydroxyalkyl ligand (**2**) and silylated derivatives thereof. α-Hydroxyalkyl **2** has been proposed as a key mechanistic branch point in Fischer–Tropsch reactions,[5,7] and is virtually a required intermediate in the Union Carbide ethylene glycol synthesis.[8] We also wish to report the X-ray structural characterization of a novel metallocyclic system which serves as the fulcrum of our syntheses.
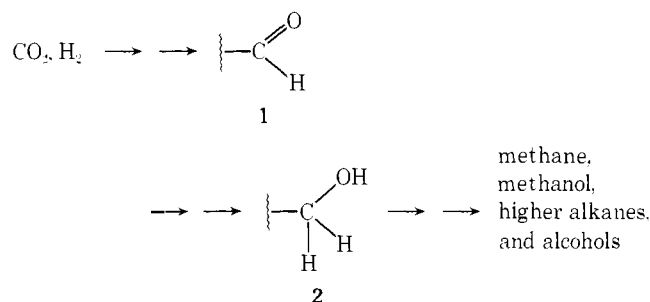
Benzoylformylmanganese pentacarbonyl (**3**, 10 mmol)[1,9] in THF (30 mL) was treated with Li(C₂H₅)₃BH (12 mmol)[10] under nitrogen. Infrared monitoring[11] suggested that an octahedral cis-disubstituted manganese tetracarbonyl product was quantitatively formed. Although we previously reported that Li(C₂H₅)₃BH attacks metal carbonyl acyls at carbon monoxide, yielding kinetically unstable anionic formyl complexes,[2] no characteristic formyl ¹H NMR resonance could be detected, even when this reaction was conducted at −60 °C in a NMR tube.

After 15 min, PPN⁺ Cl⁻ (10 mmol)[12] dissolved in CH₂Cl₂ (50 mL) was added to the reaction mixture. Solvent was removed and the residue extracted with ether (400 mL). Concentration and cooling (0 °C) afforded a yellow precipitate (two crops, 5.73 g, 6.6 mmol, 66%), which could be rendered analytically pure by first washing with cold ether and then extracting into THF. Solvent removal yielded a gold powder (46% overall) for which analytical and spectral data suggested the structure PPN⁺-**4** (Scheme I).[13]

Scheme I. Synthetic Routes to α-Silyloxy and α-Hydroxy Manganese Alkyls
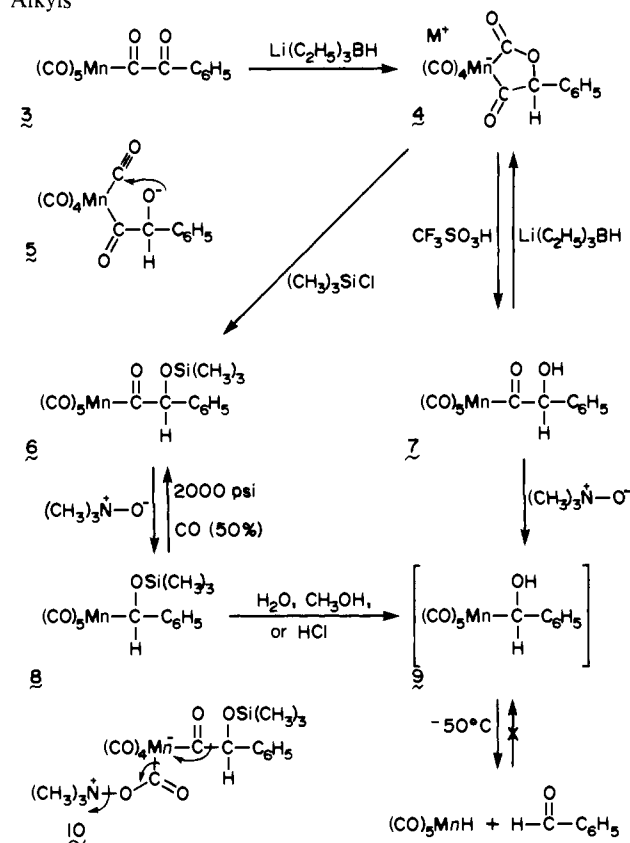
The formation of **4** is proposed to occur via intermediate **5**. In light of this unprecedented mode of metallocycle closure, an X-ray crystal structure was undertaken.

Slow recrystallization from ether–hexane afforded suitable air-stable crystals (dec pt 142–144 °C) for study. X-ray data were obtained at −160 ± 5 °C with monochromated Mo Kα (0.71069 Å) radiation on a Syntex PĪ automatic diffractometer. The general techniques employed have been previously described.[14] The unit cell was found to be triclinic, space group $P\bar{1}$ ($Z = 2$), with lattice parameters $a = 10.016$ (4), $b = 15.772$ (5), $c = 15.698$ (4) Å; $\alpha = 86.55$ (3), $\beta = 89.09$ (3), $\gamma = 118.62$ (3)°. Of 5697 reflections with $2\theta < 40°$, 2994 with $I \geq 3\sigma(I)$ were used in the final refinement. All seven phenyl rings were refined as rigid groups (C–C = 1.39 Å, C–H = 1.00 Å). A series of least-squares refinements of positional parameters of all atoms and groups, anisotropic thermal parameters of manganese and phosphorous atoms, and isotropic thermal parameters of all other nonhydrogen atoms converged to $R = 0.055$ and $R_w = 0.058$.[15] A difference Fourier map at this point revealed the location of the proton derived from Li(C₂H₅)₃BH, which was included in two further cycles of refinement. A final difference Fourier map showed no peaks larger than 0.4 e/Å. The final standard deviation of an observation of unit weight was 1.28.

The arrangement of ligands about the manganese atom is depicted in Figure 1. The metallocycle is essentially planar, and undergoes clean thermolysis (THF, 65 °C, 6 days) to PPN[Mn(CO)₅], benzaldehyde, and CO.

The metallocycle **4** undergoes two key ring-opening reactions (Scheme I). When in situ prepared Li⁺-**4** (1.01 mmol) was treated with (CH₃)₃SiCl (12 mmol), a product formed over a 2-h period. The solvent was removed and the residue column chromatographed (5% EtOAc in hexane). The product eluted rapidly and crystallized upon solvent removal (0.96 mmol, 95% yield, mp 51–53 °C). Based upon micro- and spectral analyses,[16] the silyloxyacyl structure **6** is assigned. This preparation may be executed equally well utilizing