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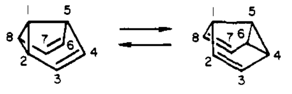
High-Resoultion NMR Studies of Solid-State Effects on Fluxional Behavior: Semibullvalene

Sir:

Over the years, NMR spectroscopy has proved to be an extremely valuable tool for the study of molecular dynamics in solution.[1] For systems undergoing rapid degenerate transformations, it is the only technique available on a routine basis which is capable of providing structural information on the nature of the relevant ground and transition states. Although certain types of molecular motion involving the movement of atoms, or groups of atoms, can be accommodated in solids,[2] the solid state could impose a barrier on a valence isomerization which would compound the usual electronic barrier. The low activation energy for the rearrangement shown coupled with minimal expected geometry change marks I as sensitive material for the study of solid-state effects on processes driven primarily by electronic, as opposed to conformational, dynamics.[3] We report here demonstration of a dramatic solid-state effect on the degenerate Cope rearrangement of semibullvalene (I), a transformation which proceeds with extreme facility in solution ($\Delta G^{\ddagger} = 5.5$ kcal/mol).[4]



I

We have used high-resolution solid-state ^{13}C NMR methods to obtain these results. The technique combines cross-polarization and high-power decoupling with "magic angle" spinning.[5] For the studies reported here, low temperatures were required, and were achieved by using an apparatus described previously.[6] Samples of I were prepared as described by Paquette and coworkers[7] and purified by gas chromatography. The liquid was loaded into a Kel-F rotor and frozen at 77 K. The cold rotor was then transferred to a precooled probe and spun at 4 kHz. Sample temperatures are quoted from measurements on the exit driving gas (helium).[6] Spectra obtained in this fashion from samples of $\sim$25 mg are shown in Figure 1. At −155 °C, semibullvalene shows five clearly resolved carbon resonances. The chemical shifts and intensities are consistent with a static structure for I and correspond closely to those reported by Anet and co-workers in solution at −160 °C with a ^{13}C frequency of 63 MHz.[4] For this reason, the original assignments are retained and shown in the figure. Retention of the liquid-state chemical shifts indicates the absence of large solid-state pertubations on the molecular electron distribution. The averaged solution chemical shifts of semibullvalene appear as arrows in Figure 1.[4] No significant change was observed in the spectrum upon raising the sample temperature to −110 °C (Figure 1). In fact, over the entire temperature range (this range was limited by the melting point of the sample at $\sim$−85 °C), no change was observed even in the line widths. Thus, the normally rapid Cope rearrangement which would be expected to average the nonequivalent carbons (2 and 8 with 4 and 6; 1 with 5) is slow in the solid state relative to the rather long time scale dictated by the smallest chemical shifts and spectrometer frequency (15.087 MHz). Using carbons 1 and 5 ($\Delta\delta = 5.1$ ppm) as guides, we conservatively estimated the rate constant at −110 °C at ≤ 400 s^{-1}. The corresponding rate constant for semibullvalene in solution at the same temperature is 2.2×10^{-5} s^{-1}![4] We have therefore conclusively demonstrated a dramatic solid-state suppression of the rate of a degenerate rearrangement which proceeds with great ease in solution and which presumably also involves little geometric distortion in the transition state.[4]

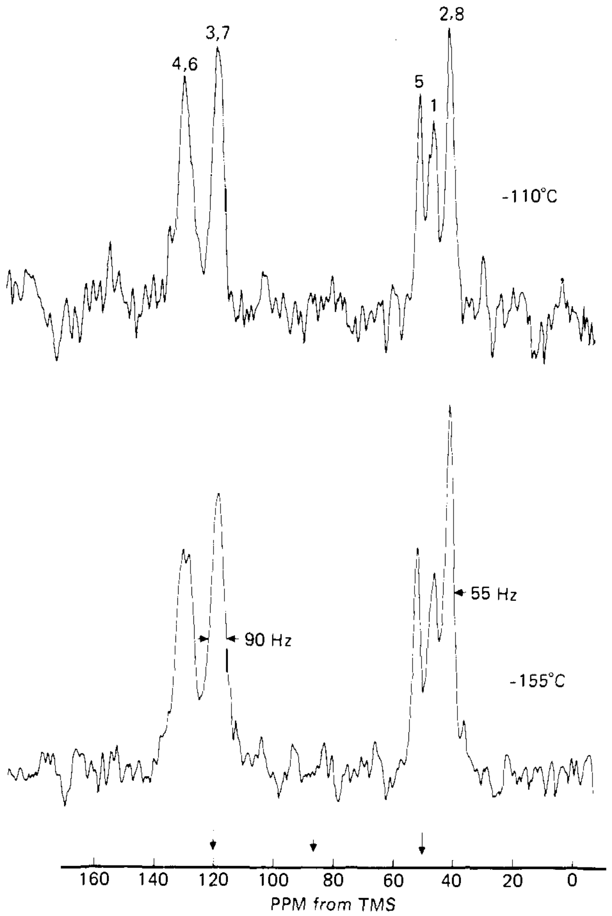


Figure 1. ^{13}C NMR spectra of solid semibullvalene, showing suppression of the degenerate Cope rearrangment. the arrows show the position of the averaged chemical shifts found in solution. Spectral parameters include: ^{13}C–^{1}H cross polarization for 5 ms with 48-kHz Hartmann–Hahn matching.[5] Number of scans (delay between scans) for −155 and −110 °C are 30700 (1 s) and 76242 (2s), respectively.

The spectral line widths are relatively large and deserve special mention. They vary from 55 to 90 Hz, and are probably due mostly to residual chemical shift anisotropy from a misalignment of the magic angle setting. This is likely since (1) olefinic carbons have a much larger anisotropy than aliphatic carbons[8] and (2) residual broadening due to misadjustment of the spinning axis is proportional to the size of the chemical shift anisotropy.[9]

The results presented here clearly bear on the prognosis for using high-resolution NMR in solids for the study of molecular dy-

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namics. Processes with very low activation energies normally require the use of low temperatures and high magnetic fields to bring the time scale of the NMR experiment into a useful range (i.e., comparable to the lifetime of the species undergoing the rearrangement).[1] Obviously, there are limitations on achieving very low temperatures with solution NMR studies; in principle, however, the possibility of doing high-resolution NMR in solids removes this constraint. In this communiction, we report an effect which indicates that even in the most favorable cases (i.e., when geometry changes along the reaction pathway from one structure to the next are minimal), it may not be possible to treat a molecular solid at low temperature as a low-temperature solution (of infinite concentration). The implication is that the activation parameters for a degenerate electronic rearrangement (or any other kind of dynamic process, for that matter) derived from a temperature-dependent study of the NMR spectrum of the solid may be more complex than its solution counterpart. The degree to which this conclusion holds will, of course, be a function of molecular structure, the phyisical nature of the sample (crystalline, glassy, etc.), the process involved, and the temperature. Nonetheless, the results presented here also suggest that it should be possible, by using this method, to distinguish in a very direct manner between equilibrating and symmetrical structures. This is particularly apropos for the study of certain semibullvalene derivatives, which, according to calculation, should have activation energies (for the Cope process) considerably lower than semibullvalene.[10] Furthermore, experiments designed to make these structural distinctions for other low activation energy processes (e.g., trivalent nitrogen inversion, rotation about carbon-carbon single bonds, pseudorotation) may now be carried out at very low temperatures in the solid state using NMR spectroscopy with near-liquid resolution. Studies of this type are in progress.

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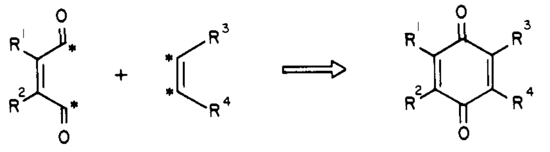
An Organotransition-Metal Synthesis of Naphthoquinones

Sir:

The quinone moiety is an important functionality in the area of bioactive natural products. It is represented in many different classes of biologically active molecules including the K vitamins,[1] ubiquinones,[2] and antibiotics and anticancer drugs.[3,4] The pervasive occurrence of the quinone functionality in nature has prompted the development of many synthetic approaches to such molecules, most of which depend upon oxidation of an appropriately substituted phenol or functionalization of a preexisting quinone.[5] A synthesis of quinones based upon the reaction of a 4-carbon maleoyl equivalent (**1**) with a 2-carbon unsaturated species (**2**) represents a potentially important, *convergent* route to substituted quinones (eq 1). If a mild and regiospecific means

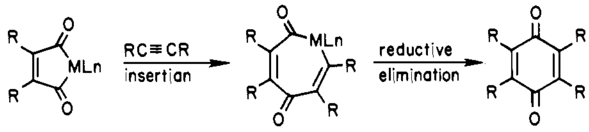


(1)

1 **2**

of joining equivalents of **1** and **2** could be found, then quinones of diverse structure could be synthesized by a common method.[6] We wish to report our preliminary results of a convergent approach to 1,4-naphthoquinones which utilizes organotransition-metal species for effecting the carbon-carbon bond formation depicted in eq 1.

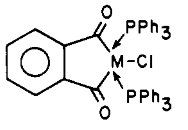
The reaction of alkynes with metal carbonyls is known to produce quinones or quinone complexes in a number of cases,[7] and the intermediacy of metallacyclopent-3-ene-2,5-diones (**3**) has been postulated to account for the quinone formation.[7c,8] The reaction is proposed to occur by insertion of an alkyne into complex **3**, giving metallacycle **4** which then undergoes reductive elimination to the quinone (eq 2). We have shown that phthaloyl metal



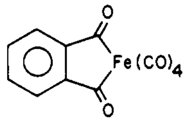
(2)

3 **4**

complexes **5**–**7** (benzo analogues of metallacyclopent-3-ene-2,5-dione (**3**)) can be conveniently synthesized in high yield from



5 M = Rh
6 M = Co



7

benzocyclobutenedione,[9] and we have now found that cobalt complex **6** and iron complex **7** react with a wide variety of alkynes to give high yields of 1,4-naphthoquinones (Table I).

Cobalt complex **6** reacts with alkynes on treatment with $AgBF_4$ in CH_3CN under mild conditions (sealed tube, 110 °C, 20–40 h), while iron complex **7** produces naphthoquinones simply on heating in CH_3CN in the presence of an alkyne (sealed tube, 100 °C, 6 h). Table I lists our current results. The iron complex appears somewhat superior to the cobalt metallacycle in that it does not require Ag^+ to induce reaction and it also cleanly reacts with a wider variety of alkynes ranging from electron rich to electron deficient. However, cobalt complex **6** does have an advantage over the iron system in three cases. The sterically demanding alkynes 2,2-dimethyl-3-pentyne (entry 7) and 1-(trimethylsilyl)-1-hexyne (entry 10) give significantly higher yields

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