

cleavage at long wavelengths produces  $W(CO)_5$  and pyridine. The former is known to react very efficiently with any ligands present in solution; when extra pyridine is present, exchange results. In pure hydrocarbon solvent, ground-state complex is the only ligand source available. The resulting  $W(CO)_4L$  eventually finds a free pyridine to produce  $W(CO)_4L_2$ . The Stern–Volmer study at 0.02 M I indicates a 5:1 value for  $k_2/k_3$ , which explains why II formation occurs even with dilute I.

Yields of  $W(CO)_4L_2$  previously have been assumed to represent how well CO cleavage competes with L cleavage in excited  $W(CO)_5L$  complexes.<sup>2–6</sup> Our results indicate that, at least for irradiation at wavelengths greater than 400 nm, most of this product arises from L cleavage followed by CO exchange. Of broader interest is the question of how general such CO exchange is.

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### Ultrahigh Resolution NMR. 1. General Considerations and Preliminary Results for Carbon-13 NMR

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The efforts to reach higher and higher magnetic fields are justified by the resulting improvements in resolution and sensitivity. Unfortunately, in the last quarter of a century the highest commercially available high-resolution magnetic field has only about doubled. While we wait another quarter of a century to get another factor of 2, we can ask if there are some interim measures that may yield much greater resolution *today*. We describe in this paper the simple instrument modifications that have yielded what we call "ultrahigh resolution" NMR, which we arbitrarily define as having been achieved when there is less than 20-mHz instrumental contribution to the line width (in  $^{13}C$  NMR). The experiments were done on a slightly modified Nicolet NT-200 NMR spectrometer at a  $^{13}C$  resonance frequency of 50.3 MHz, with a standard 12-mm probe and a sample volume of 4.2 mL. Standard single-pulse  $^{13}C$  excitation was used.

Figure 1A shows the free-induction decay (FID) of the non-protonated carbon of toluene (C-1), after four accumulations. After Fourier transformation, Figure 1A yielded an experimental best-fit Lorentzian width at half-height ( $W_{ex}$ ) of 12.6 mHz. In order to determine the instrumental contribution to  $W_{ex}$  we indirectly determined the *lower limit* to the natural line width ( $W_0$ ) from the spin–lattice relaxation time ( $T_1$ ), measured by the inversion-recovery method<sup>1</sup> with composite  $180^\circ$  pulses,<sup>2</sup>  $180^\circ$  phase alternation,<sup>3</sup> intervals between the  $180^\circ$  and  $90^\circ$  pulses in the range 5–120 s (13 values), and 400-s waiting interval between successive  $180^\circ$  pulses. The resulting best-fit least-squares  $T_1$  value was  $72.23 \pm 0.37$  s, which yielded  $1/\pi T_1 = 4.4$  mHz, a good estimate of the *lower limit* to  $W_0$ .<sup>4</sup> Therefore, the *upper limit* to the instrumental broadening ( $W_{in}$ ) of Figure 1A is 8.2 mHz. Figure 1B shows the best single-scan performance to date, with an observed line width of 11.0 mHz, which implies an upper limit to

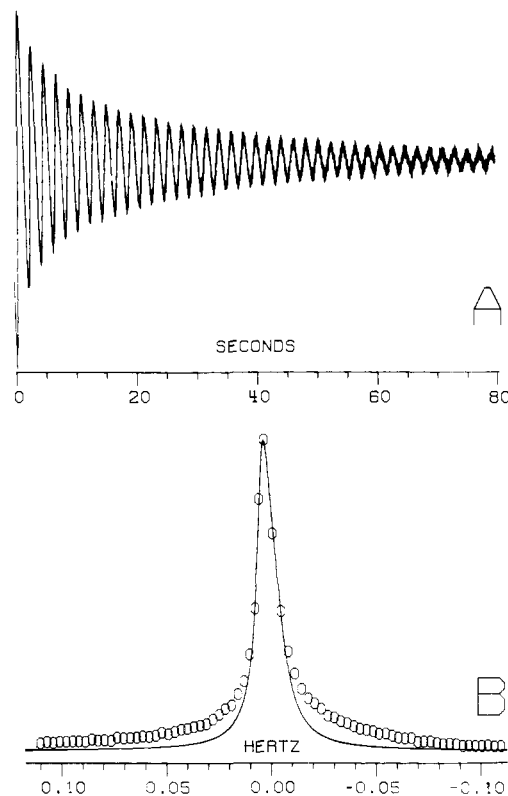


Figure 1. Proton-decoupled C-1 resonance of air-free toluene (with 20% v/v  $CD_3OD$ ) under argon at 22 °C and 50.3 MHz, an acquisition time of 163.84 s, a spectral width of  $\pm 50$  Hz (quadrature detection), and 32K total data points. (A) The initial 80 s of a free induction decay obtained after four scans with a recycle time of 163.94 s. The carrier frequency was set 0.4844 Hz from the C-1 resonance frequency. (B) Fourier-transformed signal of a free induction decay obtained after one scan. Fourier transformation was done with an additional 32K of "zero fill" data points, resulting in a simulated acquisition time of 327.68 s, which yielded a digital resolution of 3.052 mHz. The hexagons are experimental points, and the curve is the best-fit Lorentzian to the top five points, which encompass the peak to just below half-height. Zero frequency has been set at the maximum of the peak.

$W_{in}$  of only 6.6 mHz. This is more than an order of magnitude better than the 200-mHz value normally quoted for high-resolution  $^{13}C$  NMR in a 10- or 12-mm tube. Furthermore, limited digital resolution and inefficiencies of  $^1H$  decoupling have normally conspired to yield  $W_{in}$  values of 500 mHz and more.

Our studies suggest that the resolution performance of typical commercially available high-resolution superconducting magnets is much better than is generally believed and that the available resolution has been masked by broadening from chemical shift gradients caused by *temperature gradients in the sample*.<sup>5</sup> This phenomenon is not surprising if one examines available reports of the temperature dependence of chemical shifts (Table I). We eliminated temperature gradients in our probe, with (i) an increase in the flow of cooling air into the probe from about 10 L/min to about 20 L/min,<sup>6</sup> (ii) a decrease in proton decoupling power from 5 to 1.5 W and less, made possible by the efficiency of WALTZ-16 decoupling,<sup>7</sup> and (iii) improved temperature stability of the cooling air. After these modifications were made an instrumental broadening of 15 mHz and less became routinely available. Magnet shimming time and effort did not increase relative to

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**Table I.** Temperature Dependence of  $^{13}\text{C}$  Chemical Shifts<sup>a</sup>

carbon	Hz/°C	ref
hydrocarbon <sup>b</sup>	0.2	Me <sub>4</sub> Si ( $^{13}\text{C}$ )
acetone CH <sub>3</sub> <sup>c,d</sup>	0.26	CD <sub>3</sub> OD ( $^2\text{H}$ )
acetone CO <sup>e,f</sup>	0.66	CD <sub>3</sub> OD ( $^2\text{H}$ )
acetone CO <sup>f</sup>	0.99	CCl <sub>4</sub> ( $^{13}\text{C}$ )
CH <sub>3</sub> I <sup>g,h</sup>	1.31	Me <sub>4</sub> Si ( $^{13}\text{C}$ )
CH <sub>2</sub> I <sub>2</sub> <sup>g,i</sup>	2.35	cyclooctane ( $^{13}\text{C}$ )

<sup>a</sup> Converted to 50.3 MHz. Each value is not the absolute change in chemical shift with temperature but relative to the temperature dependence of the chemical shift of the internal reference (and nucleus) shown in the column labeled ref. <sup>b</sup> Typical value measured at -43 °C, taken from: Schneider, H.-J.; Freitag, W. *J. Am. Chem. Soc.* **1976**, *98*, 478-481. <sup>c</sup> Allerhand, A., unpublished results. <sup>d</sup> Measured in the range 21-27 °C. <sup>e</sup> Measured in the range 21-35 °C. <sup>f</sup> Measured in the range -80 to 90 °C, taken from Led, J. J.; Petersen, B. *J. Magn. Reson.* **1978**, *32*, 1-17. <sup>g</sup> Taken from Vidrine, D. W.; Peterson, P. E. *Anal. Chem.* **1976**, *48*, 1301-1303. <sup>h</sup> Measured in the temperature range -9 to 1 °C. <sup>i</sup> Measured in the temperature range 33-42 °C.

conventional high-resolution NMR.

In this paper we have used the nonprotonated carbon of toluene to demonstrate the feasibility of ultrahigh resolution NMR. However, a nonprotonated carbon does not place a severe requirement on proton-decoupling efficiency. In a separate report<sup>8</sup> we will show that WALTZ-16 proton decoupling, developed by Freeman and co-workers,<sup>7</sup> is an extraordinarily effective low-power proton-decoupling method for ultrahigh resolution NMR.

It would not have been practical to develop ultrahigh resolution NMR at an earlier time. First, without very efficient proton decoupling such as WALTZ-16, residual broadening from  $^1\text{H}$  scalar coupling and large temperature gradients caused by high decoupling power levels were the limiting factors.<sup>5</sup> Furthermore, ultrahigh digital resolution over the full range of  $^{13}\text{C}$  chemical shifts requires data blocks of 256K (and more) points, which would have been prohibitive until recently. What are the advantages of ultrahigh resolution over conventional high-resolution NMR? In general, one expects not only improvements in resolution but also higher signal-to-noise ratios when the instrumental contribution to the line width diminishes.<sup>9,10</sup> The degree of signal-to-noise improvement is dependent on too many parameters for discussion in this paper.<sup>9,10</sup> The degree of resolution improvement depends mainly on the value of the natural line width ( $W_0$ ). For small molecules such as toluene, with  $W_0 \lesssim 30$  mHz ( $T_1 \gtrsim 10$  s), going from  $W_{in} = 200$  to 10 mHz will yield an improvement in resolution of a factor  $\gtrsim 6$ , equivalent to going from a 200-MHz ( $^1\text{H}$ ) spectrometer to a 1200-MHz spectrometer under conventional high-resolution conditions. For larger molecules the advantage is smaller but still very significant. On the basis of published  $T_1$  values,<sup>11</sup> we expect  $W_0$  in the range 0.1-1.0 Hz for the  $^{13}\text{C}$  resonances of most molecules up to the size of steroids. At the lower end of this range, the improvement in resolution is a factor of about 3 when going from  $W_{in} = 0.2$  to 0.01 Hz. At the upper end the resolution improvement is only about 20%, comparable to the expected improvement when going from 500 ( $^1\text{H}$ ) to 600 MHz. Furthermore, in ultrahigh resolution NMR of large molecules (with  $W_0 \gtrsim 0.5$  Hz) we have  $W_{ex} = W_0$  to a very good approximation and, since  $W_0 = 1/\pi T_2$ , the observed line widths in a single spectrum may yield accurate  $T_2$  values for each resonance.<sup>12</sup>

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## Tandem Electrocyclic-Sigmatropic Reaction of Benzocyclobutenes. An Expedient Route to 4,4-Disubstituted Isochromanones

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Previous results<sup>1</sup> from our laboratory have demonstrated that the thermolysis of 1-acyl-1-alkylbenzocyclobutenes provides an efficient route to substituted isochromenes through a predominant electrocyclic reaction (ECR). In particular, upon thermolysis of the carboxylic acid **1**, the 4-alkylisochroman-3-one **4** could be obtained via the *Z* conformer of the *o*-quinodimethane **2** in a quantitative yield (Scheme I).

This reaction suggested that the ketene hemiacetal **3**<sup>2</sup> should intervene in the conversion. Assuming that the C<sub>3</sub>-OH in **3** can be substituted for allyoxy group, the resulting ketene acetal<sup>3</sup> (**6**) seems to undergo spontaneous [3,3]-sigmatropic reaction<sup>4</sup> (STR). To this purpose, the starting material should be the allyl ester **5** which would easily be accessible from the corresponding allyl alcohol and the carboxylic acid. From a practical point of view, since the resulting isochroman-3-one **7** has the quaternary carbon on a benzyl position, this strategy seems to provide an efficient route to a promising synthon for several types of natural products such as Amaryllidaceae alkaloids<sup>5</sup> or alkaloids of the Calabar bean.<sup>6</sup> (Scheme II).

In this paper we report a convenient method for constructing 4,4-disubstituted isochromanones via an unprecedented tandem electrocyclic-sigmatropic reaction of benzocyclobutenes.

The required substrates for the thermolysis were prepared from readily available 1-cyano-5-methoxybenzocyclobutene<sup>7</sup> by a three-step sequence. Alkylation (RX, LDA, HMPA, THF, -78 °C), hydrolysis (KOH, aqueous EtOH, 100 °C), and esterification (the alcohols, DCC, 4-DMAP, CH<sub>2</sub>Cl<sub>2</sub>, room temperature) yielded the corresponding esters in 80% overall yield. The thermolyses (Tables I-III) were typically carried out in a 0.03-0.05 M *o*-dichlorobenzene<sup>8</sup> solution heated at a bath temperature of 180 °C under an atmosphere of argon. The progress of the reaction was monitored by TLC analysis, and the reaction was cleanly completed within a few hours providing the expected isochroman-3-one<sup>9</sup> via a tandem ECR-[3,3]STR in excellent yield. As indicated by the representative examples in Table I, various allyl esters behave in a similar fashion, but only in the case of C<sub>1</sub>-methoxymethyl (entries 5, 6, and 12 in Table I and entry 3

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(8) The solvent was distilled under reduced pressure and degassed before use.

(9) All new compounds gave satisfactory spectral and analytical (combustion and/or high-resolution mass spectral) data consistent with the structures shown.