ethanol (200 mL) was stirred under 1 atm of hydrogen in the presence of 10% palladium on activated carbon (Aldrich Chemical Co.) for 48 h at room temperature. Thin-layer chromatography (alumina, using EtOAc–CH_3OH (10:1) as the eluant) indicated the complete disappearance of starting material. The product mixture was filtered and concentrated, yielding hydroxymethyl-18-crown-6 (1.76 g, 94%) as a colorless oil having IR and ^1H NMR spectra identical with those of an authentic sample.

Hydroxymethyl-18-crown-6 Grafted to Cross-linked Polystyrene. Hydroxymethyl-18-crown-6 (0.76 g, 2.58 mmol) dissolved in THF (40 mL) was stirred with 0.19 g (4.1 mmol) of sodium hydride under a nitrogen atmosphere at room temperature for 1 h. Chloromethylated polystyrene (1.00 g, 1% divinylbenzene–microporous, 1.76 mmol of chlorine (20% ring substitution), 20–40 mesh) was then added to the solution and the mixture refluxed without stirring for 24 h under a nitrogen atmosphere. The product mixture was cooled to room temperature and 5 mL of methanol was added. The resin was filtered, washed successively with THF (5 × 10 mL), THF–water (1:1, 3 × 10 mL), water (2 × 20 mL), and THF (10 mL) and dried under reduced pressure [12 h, 56 °C (0.1 mm)], yielding 1.400 g of polymer. For quantitative replacement of chlorine by the crown ether, the theoretical expected weight of the product is 1.462 g. The IR spectrum of the resulting resin showed a strong C–O–C band at 1200 cm^{-1} and the complete disappearance of the H–C–Cl bending vibration at 1260 cm^{-1}. Procedures similar to the above were used to graft hydroxymethyl-18-crown-6 onto a 5% ring-substituted microporous polymer.

Poly(dibenzo-18-crown-6). The procedure used for preparing poly(dibenzo-18-crown-6) was identical with that previously reported.[11]

Poly(dibenzo-18-crown-6–anisole). A solution of paraformaldehyde (3.3 g, 0.11 mol) in 30 mL of formic acid was added in one portion to a stirred solution of dibenzo-18-crown-6 (0.9 g, 2.5 mmol) and anisole (2.71 g, 25.1 mmol) in 80 mL of formic acid maintained at 60 °C. The mixture was refluxed for 5 h and the resulting gel poured into 100 mL of water, filtered, and washed with water until all traces of acid were removed. The brownish polymer was extracted (Soxhlet) for 3 days with methanol and then dried [12 h, 56 °C (0.1 mm)], affording 2.84 g of dry polymer.

Kinetic Methods. Kinetic methods used to analyze the activity of the various soluble and insoluble catalysts were similar to those previously described.[19] Culture tubes (50-mL, Corning no. 9826), containing a Teflon-coated magnetic stirring bar ($^1/_2 \times {}^5/_{16}$ in. octagonal bar with pivot ring), were used in all experiments. Pseudo-first-order rate constants were calculated from the disappearance of 1-bromooctane in the organic layer. A minimum of four aliquots was taken per reaction, and the kinetics was generally followed for at least three half-lives.

Registry No. 1a, 70069-04-4; **1b**, 76377-04-3; pentaethylene glycol ditosylate, 41024-91-3; 1,2-dihydroxy-3,3-diethoxypropane, 62334-33-2; diethoxymethyl-18-crown-6, 76377-05-4; 18-crown-6-carboxaldehyde, 76377-06-5; 1,2-dihydroxy-3-benzyloxypropane, 4799-67-1; styrene–divinylbenzene copolymer, 9003-70-7; dibenzo-18-crown-6, 14186-32-7; paraformaldehyde, 50-00-0; anisole, 100-66-3; potassium iodide, 7681-11-0; potassium cyanide, 151-50-8; potassium phenoxide, 100-67-4; 1-iodooctane, 629-27-6; 1-cyanooctane, 2243-27-8; 1-octyl phenyl ether, 1818-07-1.

Deuterium Isotope Effects in Carbon-13 Nuclear Magnetic Resonance Spectroscopy. Investigation of Tautomeric Equilibria in Enamino Ketone Systems

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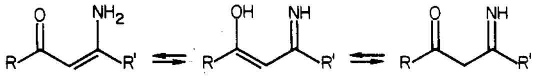
We have developed a new method by which carbon-13 NMR spectroscopy can be used to yield a qualitative picture of tautomeric equilibria. This simple-to-use procedure involves application of deuterium isotope effects.[1] The deuterium isotope effect can be manifested in several ways. The most easily recognized effects are signal broadening caused by residual C–D coupling, reduction of signal intensity by deuterium quadrapole relaxation, and deuterium isotope induced shifts.[2]

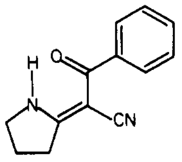
The nature of the experiment involves the examination of the sample in a coaxial NMR tube to which D_2O was added to half the solution and H_2O to the other as described by Pfeffer et al.[3] The resulting spectrum can be analyzed readily and by consideration of the deuterium isotope effects previously mentioned, information concerning the position of the deuterium can be evaluated.

We have been interested in the tautomeric properties of enamino ketones. These compounds can exist as one or some combination of the three potential tautomers shown.



1a **1b** **1c**

The determination of this type of tautomeric equilibria has been extensively studied by proton NMR with ^{15}N-labeled compounds.[4] No evidence for tautomer **1c** has ever been observed. The obvious drawback of this procedure does not allow for routine use of this method. We decided to see if deuterium isotope effects could be of some use to gain an understanding of the position of equilibrium in these systems. The three compounds studied (**2**–**4**) are shown below.



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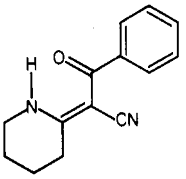

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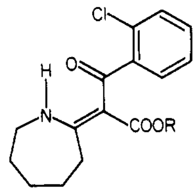

4

The results of our deuterium isotope effect investigation are exemplified by the observations given in Figures 1 and 2. Shown in Figure 1 is the deuterium isotope induced shifted spectrum of the low-field region for **3**. Isotope shifts are observed for both of the low-field resonances which can be assigned to C_1 and C_2.[5] (An isotope shift is also seen for the aliphatic carbon α to nitrogen.) Since deuterium isotope induced shifts are operative over only three bonds, the interpretation of the results is straightforward; both tautomeric forms similar to **1a** and **1b** are present in equilibrium.[2] In Figure 2 the results of the deuterium isotope effect of reduced signal intensity are obvious for carbons C_1, C_2, and C_4, due to quadrupolar and reduced dipole–dipole relaxation.[2d] This result nicely complements the isotope-shifted spectrum, confirming the tautomeric equilibrium.

A similar result was obtained for **4**. However, for **2** deuterium isotope effects were observed only for carbons C_2 and C_4, and the carbon atom α to nitrogen, strongly indicating that for **2** no tautomeric equilibrium exists. This

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(2) (a) J. Feeney, P. Partington, G. C. K. Roberts, *J. Magn. Reson.*, 13, 268 (1974); (b) R. A. Bell, C. L. Chan, and B. G. Sayer, *J. Chem. Soc., Chem. Commun.*, 67 (1972); (c) H. J. Reich, M. Jautelat, M. T. Messe, F. J. Weigert, and J. D. Roberts, *J. Am. Chem. Soc.*, **91**, 7445 (1969); (d) R. E. Echols and G. C. Levy, *J. Org. Chem.*, **39**, 1321 (1974).

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(5) We are dealing, of course, with time-averaged spectra of the "fast-exchange" type, where the observed shift of a carbon is a concentration-weighted average of the shifts of the individual species in solution.

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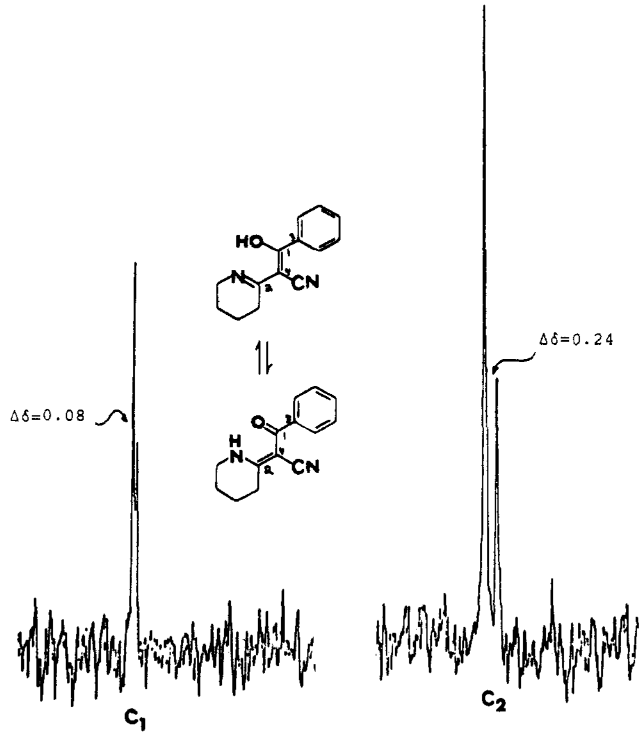

Figure 1. Low-field region for the deuterium-induced isotope shifted ^{13}C spectrum for **3**.

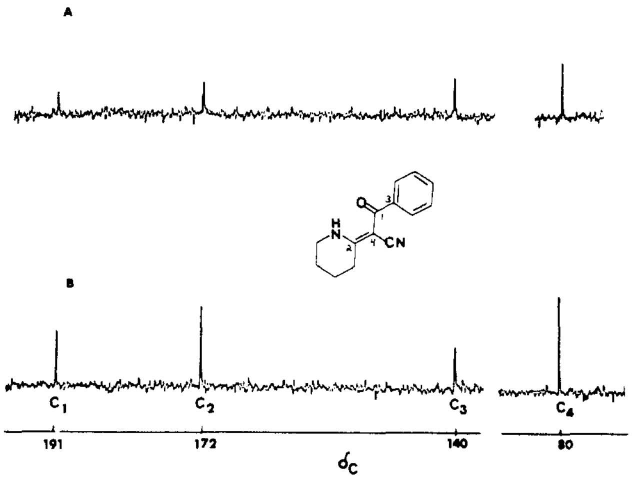

Figure 2. Deuterium-induced relaxation spectrum for **3**: (A) in Me_2SO with D_2O added; (B) in Me_2SO with H_2O added.

conclusion is consistent with that recently drawn for some β-diketone derivatives[6] and with those expected from the early work of Brown;[7] namely, the double bond prefers to be exo to a five-membered-ring system.

The utility of deuterium isotope effects and the method presented here are presently being applied to other tautomeric systems.

Experimental Section

All compounds used gave satisfactory elemental analyses and were characterized by mass spectral and infrared data as well as their NMR spectral properties. Details of the synthesis will be described elsewhere.

Natural-abundance ^{13}C NMR spectra were obtained at 25.2 MHz on a Varian XL-100-12 spectrometer system, equipped with a 620/L 16K computer in the Fourier transform mode with complete proton decoupling. General spectral and instrumental parameters were internal deuterium lock to the solvent, a pulse width of 45° and a repetition time of 1.8 s. Deuterium isotope effect spectra were performed in a manner similar to that described by Pfeffer.[3] Sample concentrations were ca. 0.5 M in dimethyl-d_6 sulfoxide, using a slight excess of D_2O to ensure exchanging the H_2O also contained in the solvent. For the isotope-shifted spectra spectral widths of 1000 Hz were used (0.25-Hz spectral resolution) and a coaxial NMR tube was employed. For the reduced-intensity spectra, spectral widths of 5000 Hz, 8K data points, were used and each portion of the material from the coaxial tube was run independently, using exactly the same conditions.

Registry No. 2, 76429-88-4; 3, 76429-89-5; 4 (R = H), 76429-90-8.

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Reduction of Alkyl Halides by Sodium Naphthalene: Proton Sources

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Alkyl anions, generated by reduction of alkyl halides by sodium naphthalene (**1**),[2] are reported to abstract protons from ethereal solvents.[3] When we tried to determine the extent of this process, however, we found it to be quite low. In fact, preliminary experiments with lauryl chloride detected no deuterium incorporation in *n*-hendecane when the solvent was tetrahydrofuran-d_4 (THF-d_4), specifically deuterated in either the α or β position.[4] We report here the results of further studies using 5-hexenyl fluoride, chosen specifically because it has been the subject of extensive study, and its behavior is presumed to be well understood.[2] The intermediate 5-hexenyl radical may cyclize to methylcyclopentyl radical, and both are reduced further by **1** to anions before forming 1-hexene and methylcyclopentane. Other products are also formed, but wehave restricted our attention to the C_6 hydrocarbons and the proton sources leading to them.

Results and Discussion

Five combinations of deuterated and undeuterated reagents were investigated. The products were analyzed for deuterium content by combined GC/MS. Table I shows the reagents, the relative yields, and the percentage of deuterium incorporation in the C_6 products for each set of conditions.

Not only are 2-hexenes formed, but they appear to be the predominant reduction products, presumably formed by protonation of the 1-propylallyl anion (**2**). Generation of **2** by reaction of 3-chloro-1-hexene with sodium metal in THF is reported to afford 95% 2-hexenes and 5% 1-hexene.[5]

The hexenes were shown to be stable in the presence of **1**-d_0 and 1-fluorohexane in THF-d_8 as that halide was reduced to form hexane (7% deuterium incorporation). In particular, no 2-hexenes were formed from 1-hexene. Thus, intermolecular proton abstraction by hexyl anion is not

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(1) Taken in part from the MS. Thesis of R.D., UNCC, 1980.

(2) J. F. Garst, *Acc. Chem. Res.*, **4**, 400 (1971).

(3) M. V. Moncur and J. B. Grutzner, *J. Am. Chem. Soc.*, **95**, 6449 (1973).

(4) T. D. Walsh, unpublished results.

(5) J. A. Pacifici, unpublished results.

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