

¹H NMR spectroscopic study of proton exchange reaction between synthesized push-pull olefinic enamines in the presence of potassium *tert*-butoxide

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Abstract: The proton exchange rates of some synthesized enamines such as 5-(cyclohexylaminomethylene)-*N,N'*-dimethylbarbituric acid, 2-(benzylaminomethylene)-5,5-dimethylcyclohexane-1,3-dione, 5-(phenylaminomethylene)-2,2-dimethylbarbituric acid and other analogues have been studied in aqueous potassium *tert*-butoxide solution and neutral conditions at 25 °C.

Keywords: Intermolecular proton exchange, Dynamic NMR, Enamines, Basic conditions.

Introduction

One of the powerful techniques for the study of the kinetic investigations is dynamic NMR spectroscopy. In the past decades NMR spectroscopy has a well-known application in studies of hydrogen exchange reactions. Proton exchange reactions are not only interesting from a theoretical view but also have a key role in wide area of chemistry [1-4]. Although different spectroscopic techniques such as IR, UV/VIS or mass spectroscopy have been used for this purpose, dynamic NMR is only technique which has found considerable application in recent years [5-7]. A proton exchange phenomenon has undeniable influence in chemical reactions because more than 80% of organic and enzymatic reactions perform it. Literature survey showed that no more investigation of proton exchange reactions of enamines has been reported in spite of their importance as reagent in organic syntheses. In continuance of our synthetic investigations, we studied

the proton exchange rates of some synthesized push-pull enamines in aqueous potassium *tert*-butoxide solution.

Results and discussion

The study of NH proton exchange reaction rate between suitable enamines could be monitored by the observation of the doublet NMR resonances of protons coupled to the exchanging protons.

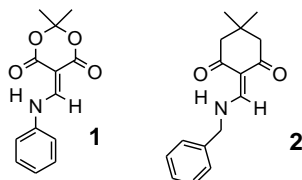
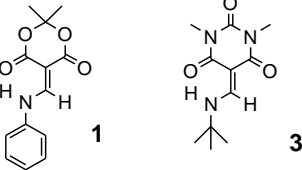
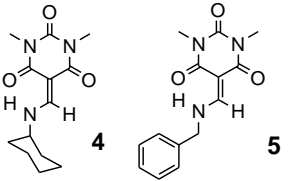
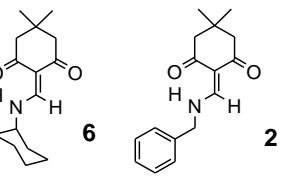
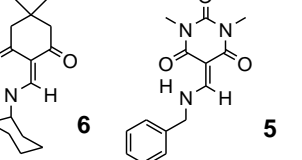
Such technique has been successfully applied to some organic compounds such as amides, hydrazines and ureas.

When proton exchanges between two components are slow relative to the ¹H NMR time scale, the spectrum of the each enamine should exhibit a 1:1 doublet for the vinylic proton, due to spin-spin coupling with the NH proton. However, if proton exchange between two components be fast the spin-spin splitting will disappear, yielding a single line. The spectra of all enamines which have been shown in table 1 were recorded for mixture and alone.

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The ^1H NMR spectrum of an equimolar solution of compounds **1** and **2** in CDCl_3 exhibits well resolved signals arising from each compound.

Table 1: Comparison of rate constant of proton exchange reaction of 1:1 ratio of enamines.

Entry	1: 1 mixture of enamines as X and Y	k (X)/k(Y)
a		$k(2)/k(1) = 8$
b		$k(3)/k(1) = 2$
c		$k(5)/k(4) = 1.1$
d		$k(2)/k(6) = 1.1$
e		$k(5)/k(6) = 2$

The spin-spin coupling constants for the vinylic protons are 14.5 and 13.4 Hz for **1** and **2**, respectively.

The chemical shifts and spin-spin coupling constants of synthesized enamines **1** and **2** have been shown in table 2.

Table 2: Chemical shifts (δ in ppm) and coupling constants (J in Hz) of enamines **1** and **2**.

Compound	δ (ppm)
1	^1H NMR (500.1 MHz, CDCl_3): δ_{H} 1.08 (6H, s, 2 CH_3), 6.56-6.92 (5H, m, C_6H_5), 7.96 (1H, d, $^3J = 14.5$ Hz, CH-NH), 10.54 (1H, br, NH).
2	^1H NMR (500.1 MHz, CDCl_3): δ_{H} 1.53 (6H, s, 2 CH_3), 2.34 and 2.36 (4H, 2 s, 2 CH_2), 4.57 (2H, d, $^3J = 6.1$ Hz, CH_2), 7.24-7.480 (5H, m, C_6H_5), 8.21 (1H, d, $^3J = 13.4$ Hz, CH-NH), 11.36 (1H, br, NH).

The ^1H NMR spectrum of an equimolar solution of compounds **1** and **2** in CDCl_3 at room temperature exhibited two sharp doublets at $\delta = 8.2$ and 8.6 ppm, readily recognizable as arising from the two CH of compounds **1** and **2**, respectively.

Dropwise addition of potassium *tert*-butoxide solution to the 1:1 mixture enamines solution of **1** and **2** leads to significant broadening of the two doublets. One of signals had different broadening from that one. Addition of the basic solution has serious effect on CH signal of compound **2**. After adding of $75 \mu\text{L}$ (0.5 M) of the base the signal of compound **2** appear as a broad single band, whereas the signal of compound **1** exhibits very little broadening.

With adding of large amount of potassium *tert*-butoxide solution the spin-spin splitting disappeared for compound **2**, whereas the signal of CH proton at compound **1** remains as a broad doublet. Hence, we can conclude that acidity of compound **2** is further than compound **1**. The results for other analogues have been summarized in Table 1.

Conclusion

In summary, as shown in Table 1 by analysis of the ^1H NMR spectra of enamines, great thermodynamic and kinetic information on proton exchange is obtained by NMR lineshape analysis. From these analyses we can compare the proton exchange rate of synthesized enamines.

Experimental

All ^1H NMR Spectra of synthesized compounds were measured on a Bruker DRX-500 AVANCE spectrometer instrument with CDCl_3 as a solvent.

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