

Tautomerism of Unconjugated Azomethines: Physical Evidence for Secondary Enamines

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IN order to understand the ultraviolet absorption spectra¹⁻³ and the chemistry of simple, unconjugated azomethines, it is important to be able to measure the extent of the potential imine-enamine tautomerism. Previous attempts to study this tautomerism by infrared spectroscopy led to the conclusion that no enamine could be detected by this method.⁴ We report how ultraviolet and n.m.r. spectroscopy can serve as potential tools to study this tautomerism.

The ultraviolet absorption spectrum of *N*-cyclohexylidenebutylamine, (I), 5.7×10^{-4} M in cyclohexane, shows a point of inflection at 220 m μ with an absorbance of 0.37. Upon addition of 10 μ l of absolute ethanol this absorbance decreases to 0.18. In pure ethanol a value of 0.07 A is observed at 220 m μ as a minimum along with a distinct $n \rightarrow \pi^*$ band of the imine at 238 m μ . Assuming that a secondary enamine would show absorption similar to that of a tertiary enamine (228 m μ , $\epsilon \sim 10^4$),⁵ we assign the absorption at

220 m μ to a measurable amount of secondary enamine tautomer. Using the absorption in absolute ethanol to represent pure imine and assuming a molar absorptivity of 10^4 for the enamine we estimate it to be present in cyclohexane solution to the extent of about 5%.

As confirmatory evidence for this tautomerism, we have been able to detect a triplet, at 4.21 δ , $J = 3$ c./sec., in the n.m.r. spectrum of (I) as a 20% solution in cyclohexane. This has been assigned to the vinyl hydrogen of the secondary enamine. Under these conditions the amount of tautomer (secondary enamine) has been estimated at 7% by comparing the area of the vinyl signal to that of a 1% solution of 1-*N*-piperidinocyclohexene in cyclohexane. The latter compound shows a triplet of identical structure for the vinyl hydrogen 4.56 δ , $J = 3$ c./sec.* *N*-Cyclohexylidenemethylamine also gave a triplet at 4.2 δ , $J = 3$ c./sec. in cyclohexane.†

The percentage enamine determined for other

* Observed using a Varian HA-100. † Observed using a Varian A-60 with 20 scans on a C-1024 time-averaging computer.

compounds by ultraviolet analysis as dilute solutions in cyclohexane were: *N*-cyclopentylidenebutylamine, 5%; *N*-cyclohexylidenebutylamine (II), less than 1%; and *N*-2,6-dimethylcyclohexylidenebutylamine, 10%. We feel that the

N-H band reported⁶ as occurring in the infrared spectrum of (II) is due to amine resulting from hydrolysis or to an overtone of the C=N stretching frequency.

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