

lated benzylboron dichloride from these reactions or from the pyrolysis of the chloroborate. In the absence of details of their work we cannot account for the difference in products, but the isolation of 84.5% tropenium and recovered cycloheptatriene in our cyclohexane reaction indicates that aromatization is not a major factor under our conditions.

(10) American Chemical Society-Petroleum Research Fund Scholar, 1960.

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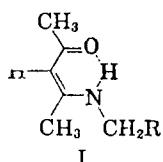
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A NUCLEAR MAGNETIC RESONANCE STUDY OF KETO-ENOL EQUILIBRIA IN SCHIFF BASES. II
Sir:

A recent paper¹ presented evidence from proton magnetic resonance that bases derived from the 2:1 condensation of a β -diketone and a diamine are present in solution to an extent $\geq 95\%$ in the ketamine form with only a small dependence of the equilibrium on solvent. The $-NH-R$ structure was inferred from spin-spin splitting of the R methylene protons ($J = 6$ cps.) by N-H. This study now has been extended to bases derived from other monoamines and β -diketones in order to explore further the apparently high stability of the ketamine over the enol-imine tautomer.

Bases formed from monoamines and simple β -diketones such as acetylacetone give rise to proton resonance spectra similar to those derived from diamines. When $R = H, CH_3, C_6H_5$ the compounds in $CDCl_3$ or CCl_4 solution exist in the ketamine form I as indicated by the vinyl signal at ~ 4.9 ppm.¹ and the splitting of the methyl or methylene protons into a doublet with $J \approx 5-6$ cps.



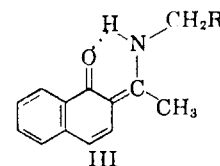
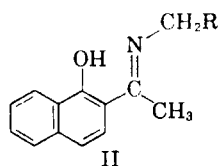
The benzyl base of dibenzoylmethane behaves similarly. No other signals attributable to the N-substituent were observable (concn. $\sim 0.4 M$) so that structure I is present to an extent $\geq 95\%$. There is no apparent solvent effect upon the equilibrium ($CDCl_3, C_6H_6, pyridine$).

These results, together with corroborative infrared studies on the above and related compounds,² offer further evidence of the greater stability of the ketamine form in aliphatic compounds as compared to either the ketimine or enol-imine tautomers. Accordingly, a search was made for other systems in which an alternate tautomer would be of comparable stability.

Derivatives of *o*-hydroxynaphthones were investigated. The tautomers II and III are possible for the base derived from 1-hydroxy-2-naphthone and a monoamine.

(1) G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 2099 (1961).

(2) N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank and D. J. Wallace, *ibid.*, **71**, 3337 (1949).



When $R = C_6H_5$ the proton resonance spectrum in $CDCl_3$ has a sharp methyl signal at 2.37 ppm., complex aromatics at ~ 7 ppm., and at 16.5 ppm. the broad signal from the acidic proton (the acidic proton in acetylacetone enol is at 15.3 ppm. in $C_6H_{12}O$). At 4.67 ppm. there is a field invariant doublet which collapses to a singlet upon deuteration of the acidic proton and is thus ascribable to the benzyl methylene group split by N-H with $J = 4.8$ cps. When $R = H$ the spectrum in either pyridine or $CDCl_3$ is analogous to that of the benzyl base. In $CDCl_3$ the methyl doublet is at 3.08 ppm. with $J = 4.4$ cps. In both compounds the stability of the keto-amine form with its chelated hydrogen-bonded ring (inferred in both cases from the presence of a highly unshielded proton) is sufficient to destroy the aromatic structure of one of the naphthalene rings. These results present some of the most direct physical evidence for such an effect. Previously, similar tautomerism in certain arylazonaphthols had been inferred from ultraviolet and infrared spectra.^{4,5,6} As expected, salicylalbenzylamine shows an unsplit methylene signal at 4.77 ppm. in $CDCl_3$.

Preliminary studies of similar bases derived from 2-hydroxy-1-naphthone and 2-hydroxy-1-naphthaldehyde indicate that the phenol-imine form predominates. When $R = H$ in the former the N-methyl signal is a sharp singlet at 3.21 ppm. in $CDCl_3$. The benzyl base of the aldehyde exhibits at 4.73 ppm. in $CDCl_3$ a broadened methylene resonance which persists in CCl_4 and pyridine.

These and other bases derived from *o*-hydroxynaphthaldehydes and *o*-hydroxynaphthones are presently under investigation and detailed results will be reported in the future.

Spectra were taken on a Varian HR-60 (at 60 or 15.1 Mc./sec.) or A-60 spectrometer using tetramethylsilane as an internal zero of reference. Bases were formed from the carbonyl compound and amine by standard procedures. Compounds were characterized by melting point or in the case of new compounds by elemental analysis. Financial support from the National Science Foundation is acknowledged.

(3) L. W. Reeves, *Can. J. Chem.*, **35**, 1351 (1957).

(4) A. Burawoy and A. R. Thompson, *J. Chem. Soc.*, 1443 (1953).

(5) E. Sawicki, *J. Org. Chem.*, **22**, 743 (1957).

(6) K. J. Morgan, *J. Chem. Soc.*, 2151 (1961), and references therein.

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THE STRUCTURE OF α -LUMICOLCHICINE—SOME EXAMPLES OF DIAMAGNETIC SHIELDING BY THE CARBON-OXYGEN DOUBLE BOND

Sir:

α -Lumicolchicine, which is formed with β -lumicolchicine and γ -lumicolchicine in the irradiation