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HINDERED INTERNAL ROTATION IN DIAZOACETONE

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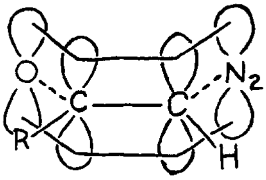
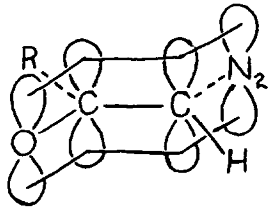
Nuclear magnetic resonance (n.m.r.) spectroscopy has proved to be a uniquely powerful tool in the investigation of structural isomerism. In addition it has permitted an evaluation of barriers to free rotation that exist in such compounds as amides, nitrites, aldoximes and nitrosamines.(2) A study of the temperature dependence of the n.m.r. spectrum of diazoacetone clearly reveals two conformational isomers, s-cis (Ia) and s-trans (IIa) owing to a barrier to free rotation about the carbon-carbon bond. Pecile et al.(3) have recently reported infrared and ultraviolet spectral evidence for rotational isomerism in diazoketones.



I s-cis



II s-trans

a) R = CH_3
b) R = C_6H_5
c) R = p-$NO_2C_6H_5$
d) R = p-$CH_3OC_6H_5$

All spectra were obtained on a Varian Associates A-60 Spectrometer equipped with a variable temperature probe and chemical shifts were measured in p.p.m. from an internal reference of tetramethylsilane. The spectrum of a 40% by weight solution of diazoacetone (4) in deuteriochloroform at 38° consists of two singlets at 5.53 p.p.m. (methine proton) and 2.08 p.p.m. (methyl protons). As the temperature is lowered the lines broaden and at 12° and below two lines for each type of proton are clearly evident indicating the lifetimes of the s-*cis* and s-*trans* forms are greater than 10^{-2} second. At -32° the areas of the low field signals, 5.32 and 5.80 p.p.m., are in the ratio of 8.4 ± 2 to 91.6 ± 2 establishing a difference in free energy of 1.14 kcal/mole between the isomers.

The parameters of the interchange reaction were determined using the method of Gutowsky et al.(5,6) Appropriate equations for unequal populations were solved assuming T_2^{-1} to be zero since the line widths of the signals were small compared to their separation when exchange was slow. Theoretical curves were obtained and the mean lifetime, τ, of the two forms of diazoacetone was determined by direct comparison of experimental curves with theoretical curves (Table I). Bovey et al.(7) have recently discussed solutions for unequal populations.

TABLE I

Mean Lifetimes of Interchanging Species

Temp., °K	τ
285.0	0.0104
280.0	0.0278
275.5	0.0348
269.5	0.0522
265.5	0.0696
255.5	0.139

The lifetimes of each species, τ_A and τ_B, were obtained from the relationships, $\tau_A = \tau/P_B$ and $\tau_B = \tau/P_A$ where P_A and P_B are the populations of the individual species. An Arhenius plot of log $1/\tau_A$ and log $1/\tau_B$ versus $1/T$°K yields a potential barrier of 9.5 ± 4 kcal/mole and a frequency factor of 10^8 - 10^9. If the interchange reaction is considered to be an equilibrium

$$A \underset{k_r}{\overset{k_f}{\rightleftarrows}} B$$

where A is the species present in highest concentration, then the rate constant $k_f = 1/\tau_A$ and $k_r = 1/\tau_B$. At the temperature of coalescence $\tau_A = 0.21$ sec. and $\tau_B \doteq 0.0114$ sec. and $k_f = 8.3$ sec.$^{-1}$ and $k_r = 87.7$ sec.$^{-1}$

The intensity of the methyl resonance at 2.11 p.p.m. is greater than that of the 2.28 p.p.m. peak; however, unequivocal assignment of high or low field peaks to a specific isomer is not possible at this time. The ratio of peaks is not appreciably altered with a change in solvent (acetone and neat liquid) or with a change in temperature below 0°. Extrapolation of linear upfield shifts of the different methine protons with an increase in temperature below 0°, indicates a 9 to 1 ratio of isomers at 38° where rapid interchange is occurring. Investigation of the temperature dependence of the ultraviolet spectrum of diazoacetone in methanol (Table II) is inconclusive as to the identity of the isomers.

TABLE II

Ultraviolet Spectrum of Diazoacetone

Temp., °C	λ_1 max	ϵ_1	λ_2 max	ϵ_2
23	246.0 mμ	9,050	270 mμ	9,300
0	246.5	8,870	271	9,440
-78	248.0	7,900	272	10,400

Examination of the C^{13} satellites of the single peak at 38° and the major peak below 0° due to the methine proton reveals no change in hybridization ($J_{C^{13}-H^1} = 199$ c.p.s.) and indicates an acidity comparable to that of furazan.(8) Morrison and Yates (9) have shown that the methine proton of diazoketones can readily be exchanged with D_2O in the presence of a variety of bases.

The temperature dependence of the n.m.r. spectra of I(b-d) and II(b-d) were investigated; however, at -40° only a slight broadening of the lines was observed. A study of other diazoketones and of the influence of equilibrium ratios on the products resulting from decomposition reactions is now in progress.

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