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MECHANISM OF THE FORMATION OF PHENYLPYRIDINIUM CHLORIDE FROM 1,7-DIPHENYL-1,7-DIAZAHEPTA-1,3,5-TRIENE

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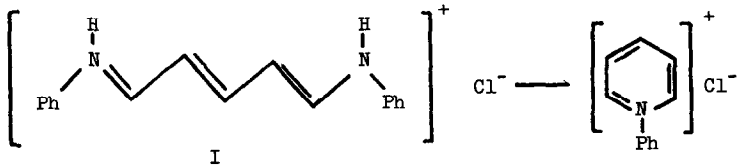
Ring-opening reactions of certain pyridinium ions (1), and ring-closures of azatrienes (2) have been well known for many years. However these facile and useful reactions have evoked little interest in their mechanisms (3). Our interest in valence isomerizations of the cis-triene to cyclohexadiene type (4) prompted us to examine these reactions, since one conceivable mechanism for both ring opening and ring closure involves such a process. We wish to report here evidence which indicates that, in at least one case, ring closure can proceed via such a mechanism.

Zincke reported (5) in 1904 that 2,4-dinitrophenylpyridinium chloride reacts with aniline to give a deep red salt which was assigned the structure I. It was also reported that I undergoes ring closure to give

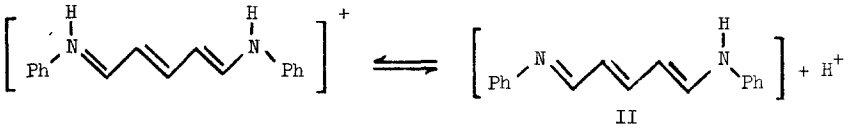


I

phenylpyridinium chloride. We have found that under conditions appropriate for kinetic studies formation and disappearance of I proceed at

comparable rates. Therefore we have chosen to isolate I (conditions where I precipitates from the reaction medium) and to study its conversion to phenylpyridinium chloride.

In anhydrous methanol this latter reaction proceeds smoothly and, within experimental error, in quantitative yield. The process is readily followed by ultraviolet spectroscopy. Initially we were surprised to find that a solution of I in methanol exhibits two peaks, λ_{max} 405, 485 mμ, whose relative intensities are concentration dependent. These two peaks were assigned to the salt form I (485 mμ) and the free base II (405 mμ). Confirmation of this assignment is provided by disappearance



II

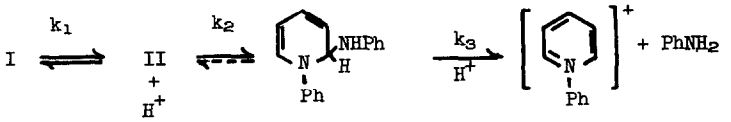
of the 485 mμ peak in the presence of excess triethylamine, and by disappearance of the 405 mμ peak in the presence of excess anilinium chloride. The value of the equilibrium constant for the above reaction is $K = 8.5 \times 10^{-8}$ moles/l. At 42.6° a 5×10^{-4} M. solution of I in methanol forms phenylpyridinium chloride by a process showing good first order kinetics, $k_1 = 8.94 \times 10^{-6}$ sec.$^{-1}$. Added neutral salts produce an autocatalytic effect which was deemed a secondary salt effect since it could be swamped by initial addition of excess aniline.

While excess aniline does not influence the rate in the absence of added salts, other stronger bases produce a notable catalytic effect. Two special characteristics of this catalysis deserve emphasis. The rate increases with added base up to the point where the base concentration is equivalent to the initial concentration of I. Thereafter the rate is independent of the base concentration. This behavior is independent of

the nature of the base, identical results being obtained with triethylamine, tributylamine and methoxide ion. In the presence of excess base the first order rate constant, $k_1' = 3.05 \times 10^{-4}$ sec.$^{-1}$ at 39.2°. Assuming that the role of the added base is to convert I completely to the reactive molecule II, one can calculate from K and k_1 that $k_1' \sim 1.0 \times 10^{-3}$ at 42.6°.

The rate of the reaction increases mildly as the solvent is changed from methanol to methanol-dioxane mixtures. An increase of 4.8 fold is observed when the mixture reaches 80% dioxane - 20% methanol. Product isolation showed the reaction was unchanged by this alteration in solvent.

All of these data are conveniently accommodated by the following mechanism. The major conformation of I is assumed to be the stretched



linear (all trans) conformer by analogy with the findings of Hoppe and Baumgartner (6) on a closely related salt. The interconversion of the linear and coiled conformations of I is expected to be rapid (7). Thus it is feasible for a small concentration of the free base with a central cis double bond to be present at equilibrium. This cis isomer undergoes valence isomerization to a dihydropyridine which loses aniline in an acid catalyzed step. The rate determining step is probably step 2, but in any event the measured rate must set a minimum for the valence isomerization. Since the cis isomer of II must be present in low concentration, the inherent rate of this valence isomerization must be of the same order of magnitude as that of the cis-dienone → α-pyran example (8).

Valence isomerization appears to constitute a second route for ring closure of azatrienes to dihydropyridines. Johnson and Rumon have reported (3) evidence for an addition-elimination mechanism. The

structural features which favor the adoption of one or the other of these two mechanisms are not immediately apparent. However the presence of a strong electron attracting substituent on the nitrogen involved in ring closure favors addition and hinders the valence isomerization.

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