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FORMATION OF PHENYLPYRIDINIUM CHLORIDE FROM 5-ANILINO-N-PHENYL-2,4-PENTADIENYLIDENIMINIUM CHLORIDE IN ACIDIC MEDIA

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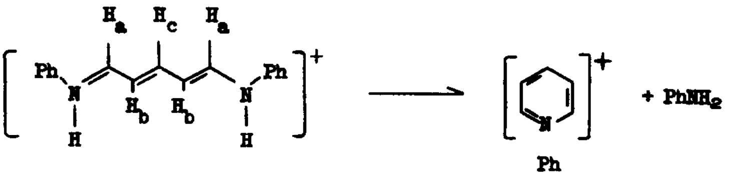
Since the discovery by Zincke[1] of the ring-opening reactions of N-(2,4-dinitrophenyl)-pyridinium ions by nucleophiles and the subsequent ring formations from the azapolyenes, these reactions have been widely employed in synthesis.[2] In his classic study Zincke found that 5-anilino-N-phenyl-2,4-pentadienylideniminium chloride (1) forms N-phenyl-pyridinium chloride (2) and aniline in both acidic and basic solution. Earlier we showed that the ring closure in basic medium is an electrocyclic reaction.[3] Here we wish to present some data which limit the mechanistic possibilities for the acid-catalyzed ring closure reaction of 1.



(1)

(2)

In methanol alone or with added triethylamine the free base form (1 minus one proton) is the sole reactive entity.[3] As the acidity of the solution is increased (added hydro-chloric acid) the rate is first depressed, passes through a minimum and then increases.

The results confirm the acid catalyzed process, but no evidence indicating direct, uncatalyzed reaction of **1** was uncovered. However methanol proved an inconvenient solvent for studies at high acid concentrations, and further kinetic study was carried out in anhydrous acetic acid (recrystallized to m.p. 16.6°). Anhydrous sulfuric acid (m.p. 10.4°) was used as catalyst and rates were followed by disappearance of the intense visible band at 480 nm. In any given run the rate is clearly first order to at least two half-lives, and the rate constants are given in Table 1. Not unexpectedly the relation between k_1 and the concentration of sulfuric acid is not linear. On the other hand a plot of log k_1 *vs* H_0[4] is roughly linear with a slope of -0.62. While this would not necessarily be expected since we are dealing with a cationic base, a parallel between H_0 and H_+ is often observed.[5]

Table 1. Rates of Ring Closure of **1** in $HOAc/H_2SO_4$ at 40°

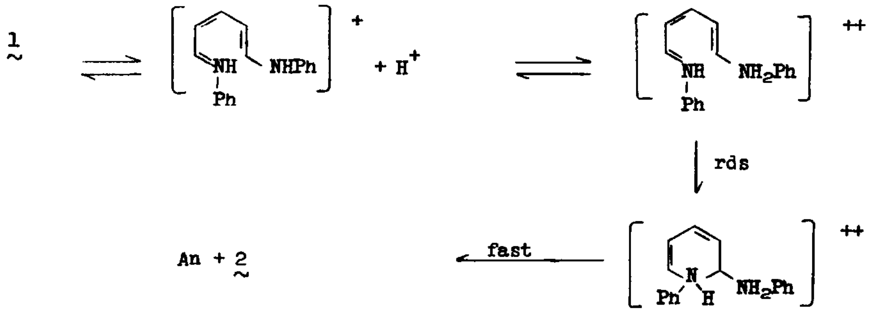
$[H_2SO_4]$(M)	k(sec.$^{-1}$)
-	2.47×10^{-5}
0.00534	5.75×10^{-6}
0.0534	2.37×10^{-5}
0.107	6.23×10^{-5}
0.287	1.01×10^{-4}

Study of aqueous sulfuric acid solutions of **1** at concentrations of acid up to 65% using uv-visible spectroscopy produced no evidence for a doubly charged species. The nmr spectrum of **1** in DMSO-d_6 is comprised of a triplet at 6.54 ($2H_b$) $J \simeq 12$ Hz, a multiplet at 7.40 (2H, *p*-H s on Ph), a pair of sharp peaks at 7.53 (8H, *o*- and m-H's on Ph), a triplet at 7.95 (H_c) $J \simeq 12$ Hz, and a doublet at 8.67 ($2 H_a$) $J \simeq 12$ Hz. The couplings are normal for the all trans configuration.[6] Addition of trifluoroacetic acid (TFA) converts the doublet at 8.67 to a triplet, and the NH protons appear as a broad doublet at ca. 12.1 ppm. Again no evidence for the presence of measureable amounts of a dicationic species was found.

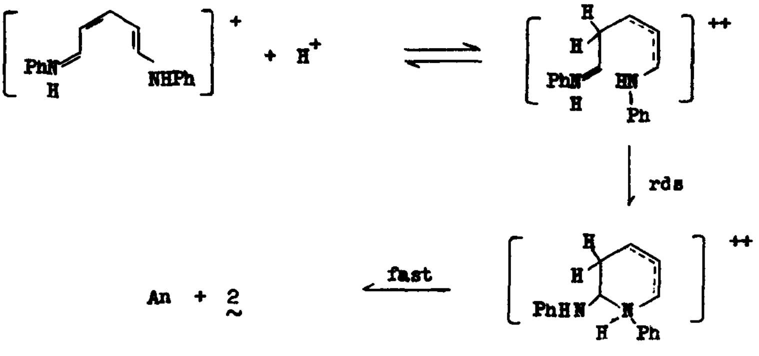
In DMSO-d_6 **1** reacts to form **2** and aniline at a moderate rate, k (40°) = 2.31×10^{-4} $sec.^{-1}$, and the rate is markedly depressed by added TFA, k (40°)~4×10^{-6} $sec.^{-1}$ from 0.3 - 2.0 M TFA. In 20% TFA-d_1/DMSO-d_6 at 24° the two H_b protons undergo exchange with k ~ 1.5×10^{-5} $sec.^{-1}$, while in TFA-d_1 the exchange rate is too rapid to measure conventionally at 0°.

The nmr spectrum of **2** in DMSO-d_6 shows a triplet at 8.44 (H_3 + H_5), a triplet at 8.90 (H_4), and a doublet at 9.46 (H_2 + H_6). The **2** recovered from ring closure of **1** in DOAc/D_2SO_4 shows only two singlets at 8.90 and 9.46. Deuterium is incorporated at C_3 and C_5 of **2**, but no other carbon-bound deuterium is found in either product. Unfortunately the rapid prior exchange of the H_b protons of **1**, renders this information mechanistically irrelevant. However measurement of the rate of reaction of **1** in DOAc/D_2SO_4 at several acid concentrations gave k_D/k_H = 2.4. This value is close to the maximum solvent isotope effect for an acid catalyzed reaction in acetic acid (2.3) calculated by the fractionation factor method.[7] The result is in accord with a mechanism involving a prior acid-base equilibrium followed by a rate determining reaction of the protonated substrate, in which no exchangeable proton can be removed.[8]

These data are in accord with two mechanisms.



An electrocyclic ring closure of the doubly charged ion having the extra proton on nitrogen, or a rate determining ring closure reaction of an intermediate dication



protonated on carbon. Direct ring closure of **1** does not occur, apparently because of the resonance stabilization. Thus the function of the acid catalyst is to reduce that stabilization.

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