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Kinetics of the Acetyl Migration in Some Adducts of Acetyl-1,4-Benzoquinones: Part III†

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The Diels-Alder adducts of acyl-1,4-benzoquinones (enediones), I, undergo base induced rearrangement in ethanolic pyridines. The effects of pyridine moiety on the reaction rate were studied.

The reaction rate was studied in different compositions of pyridine/ethanol in detail. Electronic and steric factors have great influence on the rate of rearrangement. The kinetic results are in full agreement with the proposed mechanism.

INTRODUCTION

The chemistry of the acyl-1,4-benzoquinones cyclo adducts has received an increasing interest since 1980. Many publications have appeared dealing with the synthetic studies[3–7] and also the mechanism of the[1,5] acyl migration to form the analogue hydroquinone II[3–6]. A complete kinetic study of the rearrangement of **I** → **II** has been previously carried out by our team[1,2]. This paper is concerned with the kinetics of the rearrangement process using different derivatives of pyridine, as well as different pyridine/ethanol compositions.

EXPERIMENTAL

Pyridine, α,γ-picolines, 2,6-lutidine, 2,4,6-collidine and ethanol were of spectroscopic grade as supplied by E. Merck. The adducts used were prepared and purified in our department[7,8].

Kinetic measurements

Kinetic measurements were performed on a UV Pye-Unicam SP8-200 spectrophotometer by monitoring the increase in absorbance of the hydroquinone **II** at a fixed wavelength (λ_{max} = 372 nm). The temperature was maintained constant with ±0.10°C. Stock solutions of the reactants in ethanol (1.0×10^{-3} mol L^{-1}) were prepared. 1.00 mL of the solution was transferred to a UV cell at 50°C. 1 mL (*ca.* 7.6–12.4 mol L^{-1} of pyridine or its derivatives was added to start the kinetic run. A reference cell containing 1 mL pyridine or the derivative under study and 1 mL ethanol was always used. All kinetic runs were carried out in duplicate and followed to at least three half-lives completion. In all cases, the infinity value A_∞ was determined experimentally for each run, by leaving the reaction solution at specified temperature until there was no further change in absorbance.

The rate constants for all reactions were calculated from the slopes of the plots of ln $[(A_\infty - A_0)(A_\infty - A_t)]$ *vs.* time[1] with error in $K_{obs} \leq 1$–2%. Typical plots are shown in Figure 1.

†For Part I and II, see Ref. No. 1 and 2.

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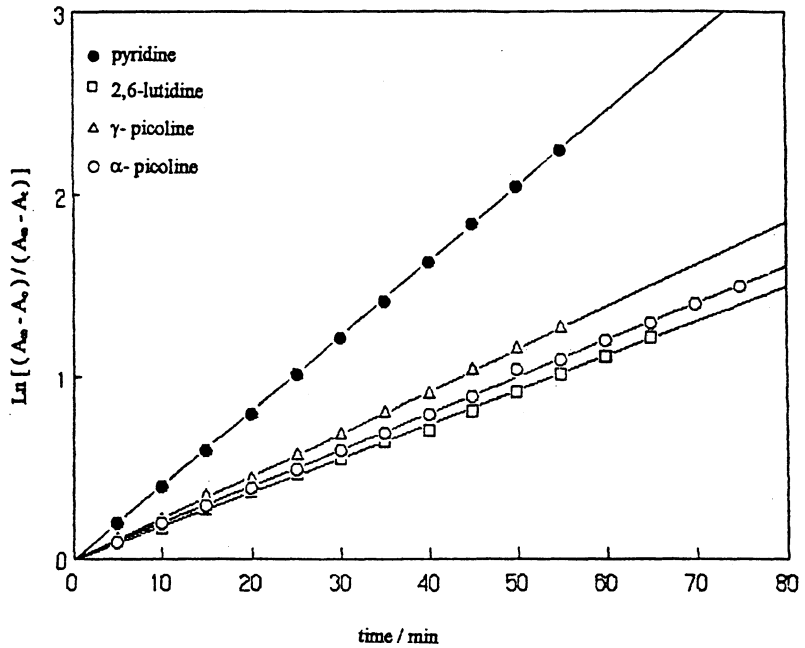
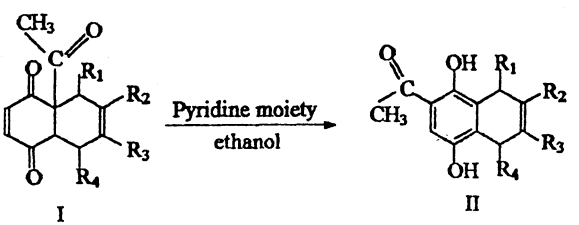


Fig. 1. First order plots for reaction of **Ib** with different pyridines at 5°C

RESULTS AND DISCUSSION

It had been shown previously[1,2] that reasonable rates of rearrangement could be obtained at a temperature range between 30–70°C. No compound other than **I** and **II** was ever detected in the products of the runs and no equilibrium between them ever existed. These observations suggest that the rearrangement proceeds clearly according to the simple stoichiometry of reaction.

The mechanism of the acyl migration is best described as shown in scheme I,



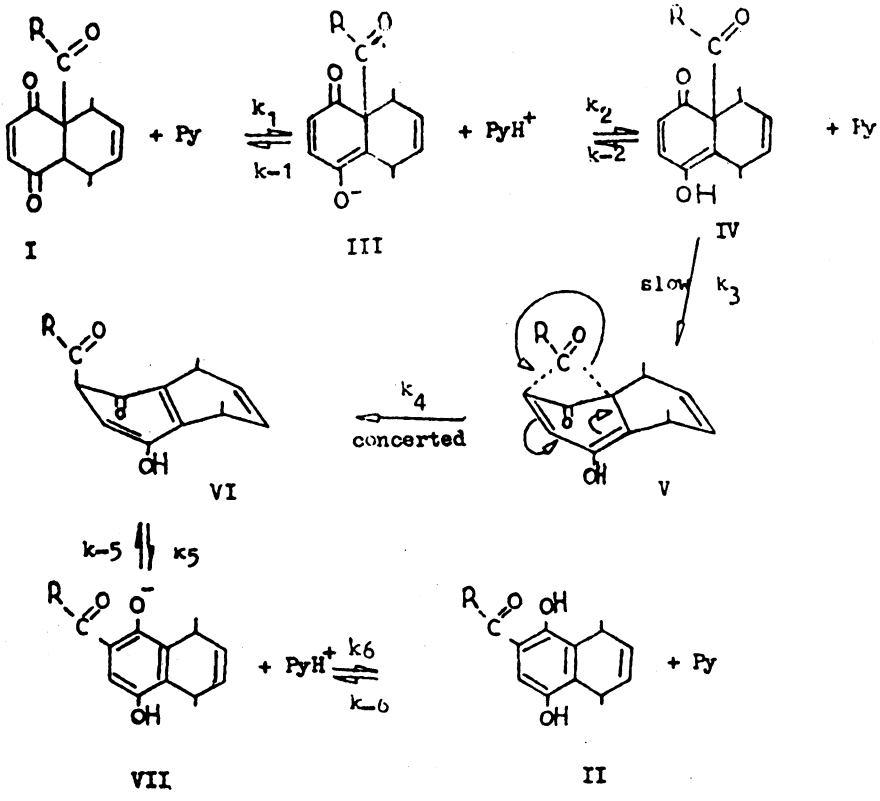
I II

I a $R_1 = R_4 = CH_3$
$R_2 = R_3 = H$

b $R_1 = R_4 = H$
$R_2 = R_3 = CH_3$

Scheme I

by an intramolecular nucleophilic substitution rather than dissociation recombination process[1,2].



Such a mechanism leads to the following rate law when a steady state intermediate concentration is assumed[1,2].

$$r = \frac{K_{eq}k_3[Py][I]}{k_3\left(\frac{k_{-1}+k_2}{k_{-1}k_{-2}}\right)+[Py]}$$

where $K_{eq} = \frac{k_1k_2}{k_{-1}k_{-2}}$

and

$$k_{obs} = \frac{K_{eq}k_3[Py]}{k_3\left(\frac{k_{-1}+k_2}{k_{-1}k_{-2}}\right)+[Py]}$$

which is in agreement with the first order behaviour of reactant **I** when high concentrations of pyridine or any of its derivatives are used.

Effect of base on the acetyl migration

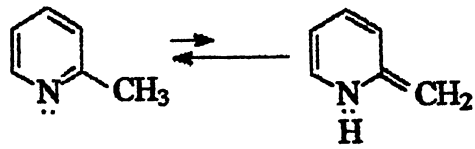
As it can be noticed from the above mechanics, pyridine moiety plays

important role in the enolization process of the adduct I. The present study is concerned with the effect of the base on the reaction rate of the adduct Ib. It is obvious that the enolization process of the adduct I is being initiated by proton abstraction at (8a) position. This, of course, depends upon the basicity of the pyridine derivatives. For this reason four methyl pyridines, in addition to pyridine itself, were used. The results, as presented in Table-1, show that the reaction rate decreases in the order of $1 > 3 > 2 > 4 > 5$.

TABLE-1
OBSERVED RATE CONSTANTS FOR REACTIONS OF **Ib** WITH DIFFERENT HETEROCYCLIC BASES AT 50°C

Base	$10^4\ k_{obs}/s^{-1}$	$t_{1/2}/s$
1. Pyridine	7.76 ± 0.03	893
2. α-Picoline	3.33 ± 0.02	2081
3. γ-Picoline	3.90 ± 0.04	1777
4. 2,6-Lutidine	3.23 ± 0.03	2146
5. 2,4,6-Collidine	very slow	—

It is expected that the presences of methyl group at position 2, 4 or 6 of the base will decrease the rate of abstraction of the proton from the adduct I. This, of course, is attributed to the resonance effect of methyl groups in pyridine ring that decreases the basicity of the nitrogen atom of the molecule toward the abstraction of proton[9], *e.g.*,



The resonance effect of the methyl group at position 4 of the pyridine ring (γ-picoline), is nearly the same as at 2-(α-picoline); but the latter may also cause a steric effect, thus restricting the approach of the pyridine ring toward proton abstraction and causing a slower reaction in α-picoline than in γ-picoline. 2,4,6-Collidine, due to resonance and steric factors inhibiting abstraction, is in line with this suggestion.

Effect of varying percentage of pyridine on the rate of reaction

In order to prove that rate dependence on pyriidne concentration exists, runs were carried out at 50°C for the adduct **Ia** over a range of different pyridine compositions. The differences in rate constants are shown in Table-2.

As in our previous study[1], the rate of reaction passes throgh a maximum value at 25% vol. composition, as shown in Figure 2. The rate of reaction, as previously reported[1], is dependent on the ratio of $[Py]/[PyH^+]$, which in turn depends upon the ethoxide ion in solution. Thus, the increase in free pyridine concentration with decreasing ethanol content will lead to better enolization chance causing a faster

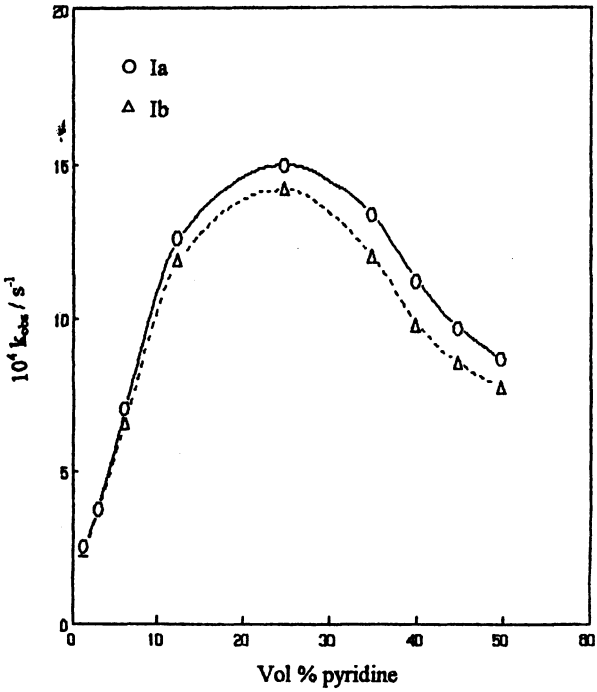


Fig. 2. Dependence of k_{obs} on pyridine concentration at 50°C

reaction at 25% pyridine composition. But when the composition changes from 25–50% pyridine, the concentration of PyH^+ drops sharply due to the decrease in ethanol content leading to a decrease in the rate of reaction.

TABLE-2
OBSERVED RATE CONSTANTS FOR **Ia** AT 50°C USING DIFFERENT PYRIDINE COMPOSITIONS IN ETHANOLIC REACTION MIXTURE

% Composition* of pyridine	Vol. % Py	Py/Ia mole ratio	$10^4 K_{obs}/S^{-1}$	$t_{1/2}$/S
42.0	50.00	12400	8.72	795
37.8	45.00	11160	9.71	714
33.6	40.00	9920	11.25	616
29.4	35.00	8680	13.34	520
21.0	25.00	6200	15.00	462
10.5	12.50	3100	12.60	550
5.3	6.25	1550	7.10	976
2.6	3.13	775	3.82	1814
1.3	1.56	387	2.60	2665

*% Composition Py = $10^2 X_{py}/(X_{py} + X_{ethanol})$

The differences in rates of rearrangement between **Ia** and **Ib**, as shown in Fig. 2, may be attributed to the steric hindrance caused by the methyl group in **Ia**. This is due to the 1,3 interaction between methyl group at position 8 and the acetyl group[9]. This interaction, together with the interaction between the acetyl group and the neighbouring methyl group at position 5, will enhance to acyl migration to position 2, thus destabilizing the intermediate and leading to a faster reaction.

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