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The Reactivity of 2,4,6-Tirphenylpyridinium Ylids

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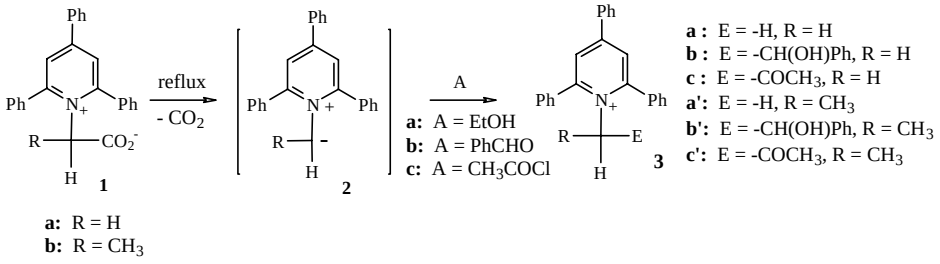
Abstract: Triphenylpyridinium ylid **2**, generated by the decarboxylation of betaine **1**, were noted to react with acetyl chloride, chloroform or acetone to form addition-elimination product and proton extraction - carbanion addition products, respectively. The reaction with chloroform was determined as pseudo first order from kinetic experiments. The values of k_{obsd} and $t_{1/2}$ for decarboxylation at 20, 40 and 50°C were calculated to be 4.6 x 10^{-4}, 8.8 x 10^{-3}, 2.8 x 10^{-2} min^{-1} and 1.5 x 10^{3}, 78, 24 minutes, respectively.

Keywords: Pyridinium ylid, pyridinium betaine, 4-H pyridine, kinetic experiment.

Nitrogen ylids[1,2] are reactive species which are not studied as vastly as phosphorus or sulfur ylids[3]. We have been studying the chemistry of pyridinium ylids and in a previous paper[4], we reported the generation of ylid **2** *via* decarboxylation of pyridinium betaine **1** and then studied the reaction with certain electrophile. In this work, we wish to report other type of reactions that observed and the reactivity of **2**.

Scheme 1



a: R = H
b: R = CH_3

In addition to the proton extraction reaction with ethanol, addition reaction with benzaldehyde, a new type of addition-elimination reaction was noted. The reaction of pyridinium betaine **1** with acetyl chloride in boiling dichloromethane afforded adduct **3c'** as white solid (65 %). The reactions required that reagents be freshly distilled otherwise significant amount of protonation product **3a′** was formed.

Besides the above nucleophilic reactions, unusual phenomena were noted in which **1** were converted to 4-H pyridines **4** (λ_{max} = 307 and 300 nm for **4a** and **4b**, respectively)

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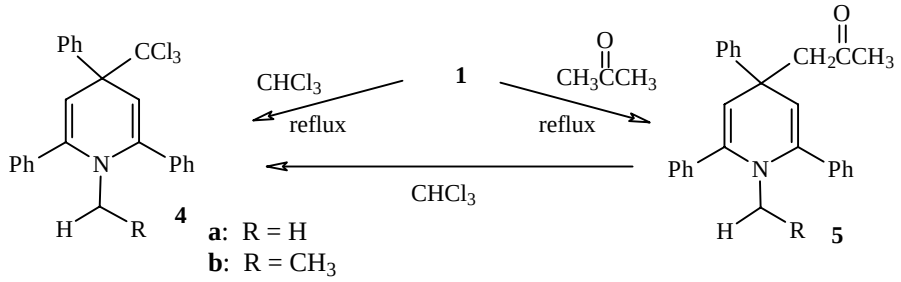
in boiling chloroform (**Scheme 2**). Small amount of protonation product **3a** and **3a'** were observed as side product with ratio around 1:3 and the amount depending upon the purity of chloroform. Chloroform of analytical grade or freshly distilled provided higher yields of **4**. The ^{1}H spectra of **4** showed significantly high field chemical shifts of alkyl group; ^{13}C NMR also showed high field shift of 4-C pyridine ring carbon and appearance of CCl_3 peak at 77.21 and 77.49 ppm for **4a** and **4b**, respectively. The formation of **4** was rationalized by the back attack of the resulting counterion CCl_3^- to the 4-position of pyridinium moiety. This postulate was supported by an independent synthesis of **4b** in which **3a'** was treated with $NaOCH_3$ and $CHCl_3$ at 0°C for 2 hours and **4b** was obtained as white solid (m.p. 130-32°C, 87 %) (**Scheme 3**). It was interesting to note that no methoxy adduct **6** was isolated and which probably due to the labile C-OCH_3 bond. It was further noted that **1** in boiling acetone produced similar result and adduct **5** was formed (**Scheme 2**). This type reactions diminished the probability that dichlorocarbene was involved for the formation of **4** *via* intermediate **7**. Dichlorocarbene was probably not formed due to the existence of electron deficient pyridinium system. The acetone adduct **5b** was noted to transform gradually to the chloroform adduct **4b** in the presence of $CHCl_3$ as monitored by ^{1}H NMR. The structures of **4b** and **5b** were characterized by unusually high chemical shifts of ethyl group in ^{1}H NMR where CH_3 peaks appeared at 0.28 and 0.50 ppm for **4b** and **5b**, respectively. The high field chemical shifts of CH_3 might suggest that the phenyl groups were oriented perpendicular to the pyridine ring as shown in structure **4'b** (**Scheme 3**) and that ethyl group lied between 2,6-phenyl groups and was affected by the ring current.

Kinetic experiments for the decarboxylation of **1a** in chloroform were investigated by temperature-varied ^{1}H NMR technique. The experiments were performed by examining the progress of disappearance of the methylene group of **1a**. Reactions under different temperatures (0, 20, 40 and 50°C) were explored. The plot of the ln (concentration), the integration of methylene group relatively to the internal standard of cyclohexane, *versus* time gave straight line (**Figure 1**) which indicated that decarboxylation of **1a** was the determining-step in the reaction. The reaction at 0°C took place extremely slowly and no significant change was noted after 2 weeks. The values of k_{obsd} and $t_{1/2}$ for decarboxylation of **1a** in chloroform at 20, 40 and 50°C were calculated to be 4.6×10^{-4}, 8.8×10^{-3}, 2.8×10^{-2} min^{-1} and 1.5×10^{3}, 78, 24 minutes, respectively.

Scheme 2



Scheme 3

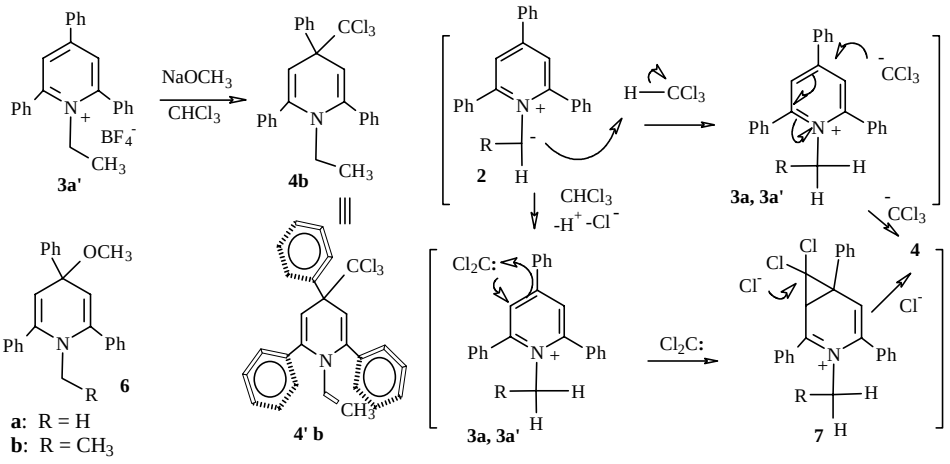
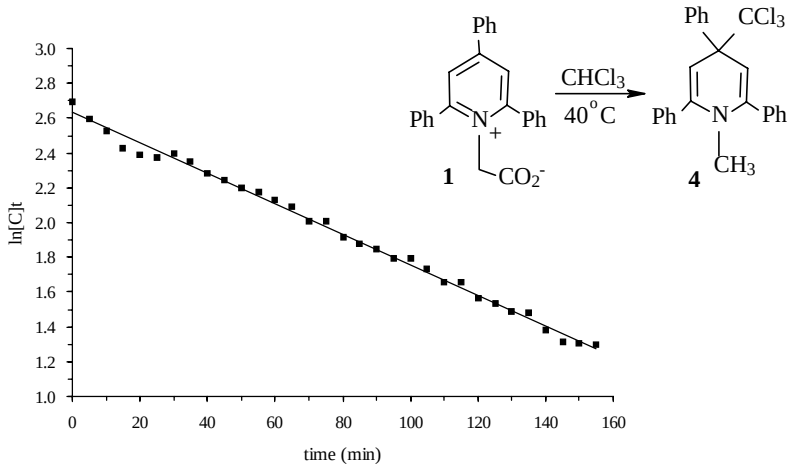


Figure 1



In summary, new types of reactions were observed for pyridinium ylid **2** which was generated *in situ* from the decarboxylation of pyridinium betaine **1**. The decarboxylation process is pseudo first order and k_{obsd} is increased with increasing temperature. Ylids **2** are relatively reactive species which function as bases or nucleophiles depending upon the reaction environment and the *para*-position of the ring may be attacked by certain species to give 4H-pyridines.

Acknowledgment

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References and Notes

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5. NMR data of compound **1a** (200 MHz for ^{1}H NMR and 50 MHz for ^{13}C NMR, in $CDCl_3$, δppm): ^{1}H NMR: 4.70 (s, 2H, CH_2), 7.58 (m, 9H, Ph), 7.75-7.79 (m, 6H, Ph), 7.91 (s, 2H). ^{13}C NMR: 60.27 (CH_2), 125.72, 127.70, 128.69, 129.31, 129.80, 131.05, 132.10, 132.57, 133.78, 154.64, 156.72, 166.64 (CO). DEPT, CH_3 carbons: none; CH_2 carbons: (1 peak) 60.27; CH carbons: (7 peaks) 125.72, 127.70, 128.69, 129.31, 129.80, 131.05, 132.57. Compound **1b**: ^{1}H NMR: 1.17 (d, 3H, J = 7.2 Hz, CH_3), 5.49 (q, 1H, J = 7.2 Hz, CH), 7.58 (d, 9H, J = 2.8 Hz, Ph), 7.75 (m, 6H, Ph), 7.85 (2H, s). ^{13}C NMR: 18.28 (CH_3), 69.46, 127.68, 129.14, 129.20, 129.30, 129.81, 130.86, 132.06, 133.74, 133.79, 153.96, 153.98, 170.06 (CO). DEPT, CH_3 carbons: (1 peak) 18.28; CH_2 carbons: none; CH carbons: (8 peaks) 69.46, 127.68, 129.14, 129.20, 129.30, 129.81, 130.86, 132.06. Compound **3a**: ^{1}H NMR: 3.86 (s, 3H, CH_3), 7.56-7.58 (m, 9H, Ph), 7.75-7.78 (m, 6H, Ph), 7.84 (s, 2H). Compound **3a'**: ^{1}H NMR: 0.93 (t, 3H, J = 6.8 Hz, CH_3), 4.45 (q, 2H, J = 6.8 Hz, CH_2), 7.51 (m, 9H, Ph), 7.65-7.79 (m, 6H, Ph), 7.81 (s, 2H). Compound **3b**: ^{1}H NMR: ($CDCl_3$) 4.63 (m, 3H, CH_2 and CHOH), 6.44 (d, 2H, J = 5.8 Hz, Ph), 7.06 (m, 3H, Ph), 7.61 (m, 9H, Ph), 7.76-7.79 (m, 4H, Ph), 7.89 (m, 2H, Ph), 8.07 (s, 2H); (DMSO) 4.40-4.75 (m, 3H, CH_2 and CHOH), 6.50 (d, 2H, J = 5.8 Hz, Ph), 7.20 (m, 3H, Ph), 7.70 (m, 9H, Ph), 7.90 (m, 4H, Ph), 8.35 (m, 2H, Ph), 8.62 (s, 2H). ^{13}C NMR: ($CDCl_3$) 61.1 (CH_2), 71.2 (CHOH), 125.2, 127.2, 128.0, 128.2, 128.9, 129.3, 129.8, 131.3, 132.1, 132.4, 133.0, 133.6, 134.2, 139.8, 156.6; (DMSO) 61.0 (CH_2), 70.2 (CHOH), 125.1, 126.2, 129.5, 130.0, 130.5, 130.8, 131.0, 131.2, 132.0, 132.5, 133.0, 133.9, 140.7, 155.0. Compound **3b'**: ^{1}H NMR: 1.45 (d, 3H, J = 7.2 Hz, CH_3), 4.46 (s, 1H, OH), 5.14 (m, 1H, CHN), 6.10 (m, 1H, CHO), 6.84 (m, 2H, Ph), 7.45 (m, 3H, Ph), 7.60 (m, 9H, Ph), 7.75-7.80 (m, 6H, Ph), 7.90 (s, 2H). Compound **3c'**: ^{1}H NMR: 1.37 (d, 3H, J = 7.2 Hz, CH_3), 1.92 (s, 3H, $COCH_3$),5.50 (q, 1H, J = 7.2 Hz, CHN), 7.75 (m, 13H, Ph), 8.30 (m, 2H, Ph), 8.52 (s, 2H, CH). Compound **4a**: ^{1}H NMR: 2.60 (s, 3H, CH_3), 5.58 (s, 2H, CH), 7.41 (d, 9H, J = 4 Hz, Ph), 7.76 (d, 4H, J = 7.8 Hz, Ph), 8.04 (m, 2H, Ph). ^{13}C NMR: 37.71, 60.21, 77.21, 103.46, 126.93, 127.33, 128.70, 129.23, 129.56, 129.64, 137.21, 143.44, 146.05. Compound **4b**: ^{1}H NMR: 0.28 (t, 3H, J = 7.2Hz, CH_3), 3.10 (q, 2H, J = 7.2 Hz, CH_2), 5.76 (s, 2H, CH), 7.41 (d, 9H, J = 4 Hz, Ph), 7.76 (d, 4H, J = 6.2Hz, Ph), 8.21 (dd, 2H, J_1 = 7.8 Hz, J_2 = 1.4 Hz, Ph). ^{13}C NMR: 13.79, 26.98, 43.23, 77.49, 107.48, 127.45, 128.91, 129.00, 129.11, 129.25, 129.78, 137.74, 145.26, 145.45. Compound **5b**: ^{1}H NMR: 0.50 (t, 3H, J = 7.2 Hz, CH_3), 2.03 (s, 3H, CH_3), 3.15 (s, 2H, CH_2), 3.10 (q, 2H, J = 7.2 Hz, CH_2), 5.24 (s, 2H, CH), 7.42 (d, 9H, J = 4 Hz, Ph), 7.75 (d, 4H, J = 6.2 Hz, Ph), 8.20 (dd, 2H, J_1 = 7.8 Hz, J_2 = 1.4 Hz, Ph).

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