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Preparation and Reactions of Pyridinium Ylids *via* Decarboxylation of Pyridinium Betaines

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Abstract: Pyridinium ylids **4** were generated as reaction intermediates from the decarboxylation of pyridinium betaines **3**, which were prepared from the reactions of α-amino acid ester hydrochlorides with 2, 4, 6-triphenylpyrylium tetrafluoroborate. Protonation, addition and substitution reactions of **4** with electrophiles were studied in this paper.

Keywords: Pyridinium betaine, pyridinium ylid, decarboxylation, electrophile.

Ylids are charged organic compounds with characters differ from regular organic compounds[1]. Nitrogen ylids, due to their instabilities, are not studied as vastly as phosphorus or sulfur ylids[2]. Nitrogen ylids are generally obtained by removing proÿSMB àÁ(s with base[3,4]. In this work, we tried to study the generation of pyridinium ylids **4** *via* decarboxylation process in neutral condition and study the related reactions with electrophiles.

The precursor of pyridinium ylids **4**, pyridinium betaines **3**, were prepared from α-amino acid as shown in **Scheme 1**. Amino acids **1** were easily converted to the ethyl ester hydrochlorides **6** by treatment with anhydrous ethanol and gaseous HCl. The reaction of **6** and pyrylium salt **2** in the presence of triethylamine and acetic acid provided pyridinium esters **7** as white solid (mp 195-7, 115-7, 118-9, 202-4°C for **7a-d**, respectively) and in good yields (87-92 %,). It was noted that MS spectra of **7** showed unusual phenomena in which $(M\text{-}BF_4\text{-}1)^+$ ions were observed for this series of compounds. Ylid-like transients **7'** (**Scheme 1**) were supposed to be formed during the electron bombarding process and which were attributed to the weak α-H-C bond. Hydrolysis of **7** in potassium hydroxide ethanol solution (room temperature, 2 hours, monitored by TLC) afforded pyridinium betaines **3** as light yellow powder in fair yields (72-80 %).

In the presence of ethanol at 80°C, **5a-b** were formed from the decarboxylation of pyridinium betaines **3a-b** (92-95 %, **Scheme 2**). The same results were observed for the reactions with other protic solvents. The spectra of **5a-b** were the same as that prepared by an alternative route[5] in which pyrylium salt **2** was reacted with aqueous methylamine

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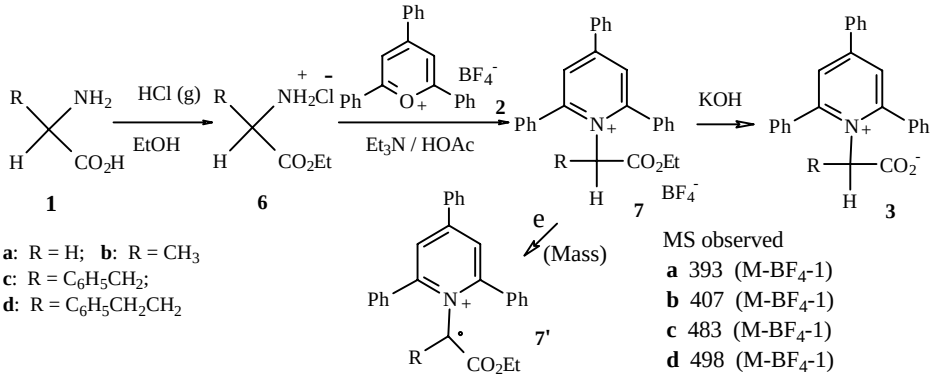
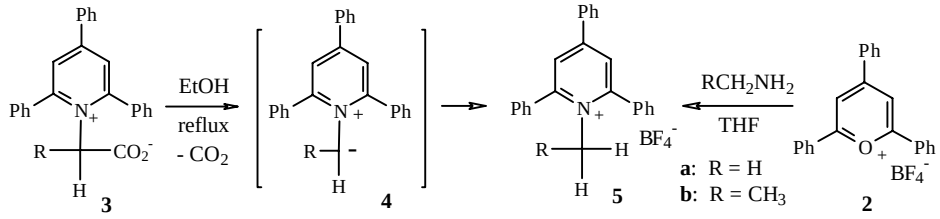
and ethylamine, respectively (**Scheme 2**) in THF and stirred 5 hours at room temperature.

Scheme 1



Betaine **3** were relatively stable at 20°C and the decarboxylation was noted to occur when the temperature was raised above 40°C. The results suggested that ylid **4** is not a stable species and which functioned as a base to abstract proton from other molecules.

Scheme 2

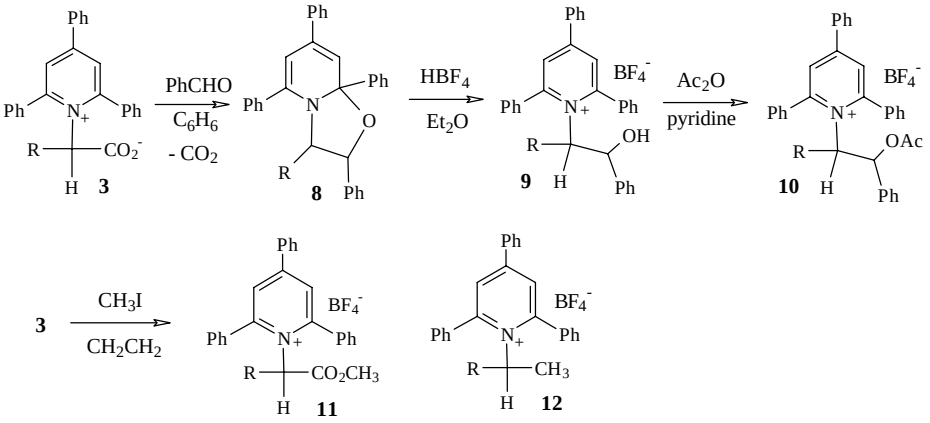


The addition reactions of the ylids were observed when **3** were treated with benzaldehyde in boiling benzene for a couple of hours (**Scheme 3**). After evaporation of solvent and extraction with ether, the cyclization product **8** was obtained. The product is a relatively unstable compound probably due to the steric hindrance and the loss of aromaticity. The structure of **8** was suggested by ^{1}H and ^{13}C NMR spectra in which the signal of symmetrical triphenylpyridine moiety was lost and complicate peaks appeared as compared with **3** and **9**. When **8** was treated with HBF_4 in ether, white precipitate was obtained and which was identified as the benzaldehyde adduct **9**. For the purpose of structure verification, **9a** (mp 137.5-139°C) was converted to acetate **10a** (mp 202-203.5°C) by treatment with acetic anhydride and pyridine in chloroform. The addition reactions required that benzaldehyde and solvents should be relatively pure. The presence of proton source might lead to formation of protonation product **5**.

The reaction of **3** with iodomethane in boiling dichloromethane afforded ester **11** and no decarboxylation adduct **12** was noted. The structure of **11** was confirmed by

alternative reaction of pyrylium salt **2** and glycine methylester hydrochloride with the same procedure as that for ester **7**. The phenomena were attributed to the high reactivity of iodomethane which reacted readily with the bared carboxylic group.

Scheme 3



In summary, pyridinium ylids **4** can be generated from the decarboxylation of pyridinium betaines **3** in neutral and mild condition. Ylids **4** were relatively unstable and existed as reaction intermediates which, after generated from **3**, abstracted proton from protic solvent and reacted with benzaldehyde to form addition product.

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References and Notes

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6. NMR data of compound **3a**: (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 **3b**: ^{1}H NMR: 1.17 (d, 3H, J = 7.2 Hz, CH_3), 5.49 (q, 1H, J = 7.0 Hz, CH), 7.58 (d, 9H, J = 2.8 Hz, Ph), 7.75 (m, 6H, Ph), 7.85 (s, 2H). ^{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 **5a**: ^{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). ^{13}C NMR: 44.79 (CH_3), 125.78, 127.95, 129.13, 129.37, 129.65, 131.13, 131.95, 132.80, 134.09, 155.65, 157.09. Compound **5b**: ^{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). ^{13}C NMR: 14.94 (CH_3), 50.46 (CH_2), 126.69, 128.04, 128.96, 129.23, 129.57, 130.91, 131.95, 132.67, 133.88, 155.49, 156.36. Compound **7a**: ^{1}H NMR: 1.04 (t, 3H, J = 7.2 Hz, CH_3), 4.02 (q, 2H, J = 7.2 Hz, OCH_2), 5.09 (s, 2H, CH_2N), 7.57 (m, 9H, Ph), 7.59-7.79 (m, 4H, Ph), 7.82 (m, 2H, Ph), 7.96 (s, 2H). Compound **7b**: ^{1}H NMR: 1.14 (t, 3H, J = 7.2 Hz, CH_3), 1.41 (d, 3H, J = 7.2 Hz, CH_2), 4.08 (q, 2H, J = 7.0 Hz, CH_2), 5.48 (q, 1H, J = 4.0 Hz, CH), 7.51 (m, 9H, Ph), 7.65-7.75 (m, 6H, Ph), 7.84 (s, 2H). Compound **7c**: ^{1}H NMR: 1.20 (t, 3H, J = 7.2 Hz, CH_3), 2.87 (m, 1H, PhCHH), 3.45 (dd, 1H, J = 7.2 Hz, 3.8 Hz, PhCHH), 4.09 (q, 2H, J = 7.0 Hz, OCH_2), 5.63 (dd, 1H, J = 8.2 Hz, 3.8 Hz, CH), 6.76 (d, 2H, J = 4.0 Hz, Ph), 7.08 (m, 3H, Ph), 7.54-7.57 (m, 9H, Ph), 7.82 (m, 4H, Ph), 7.85 (d, 2H, J = 7.6 Hz, Ph), 7.94 (s, 2H). Compound **7d**: ^{1}H NMR: 1.20 (t, 3H, J = 7.2 Hz, CH_3), 1.94 (m, 2H, CH_2), 2.39 (m, 2H, CH_2), 4.16 (q, 2H, J = 7.2 Hz, OCH_3), 5.34 (dd, 1H, J = 7.2 Hz, 3.8 Hz, CH), 6.91 (d, 2H, Ph), 7.09 (d, 3H, Ph), 7.50 (m, 9H, Ph), 7.55-7.80 (m, 6H, Ph), 7.87 (s, 2H). ^{13}C NMR: 13.71 (CH_3), 32.83 (CH_2), 33.20 (CH_2), 63.32 (OCH_2), 68.17 (CHN), 126.32, 127.77, 128.33, 128.41, 128.49, 129.05, 129.10, 129.55, 131.27, 132.20, 132.44, 133.69, 138.58, 156.75, 156.85, 168.12. DEPT: CH_3 carbons: (1 peak) 13.71; CH_2 carbons: (3 peaks) 32.83, 33.20, 63.32; CH carbons: (11 peaks) 68.18, 126.32, 127.77, 128.33, 128.41, 128.49, 129.05, 129.10, 129.55, 131.27, 132.44. Compound **9a**: ^{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 **9b**: ^{1}H NMR, δ 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 **10a**: ^{1}H NMR: 1.97 (s, 3H, CH_3), 4.95 (m, 2H, CH_2), 5.70 (m, 1H, CH), 6.40 (m, 2H, Ph), 7.05 (m, 3H, Ph), 7.55-7.65 (m, 9H, Ph), 7.80 (m, 6H, Ph). 7.95 (s, 2H). ^{13}C NMR: 21.04 (CH_3), 58.21 (CH_2), 73.38 (CHO), 125.97, 128.05, 128.15, 128.92, 129.30, 129.75, 130.90, 131.30, 131.50, 132.45, 135.47, 157.02, 158.11, 170.24 (CO). Compound **11a**: ^{1}H NMR: 3.55 (s, 3H, CH_3), 5.12 (s, 2H, CH_2), 7.59 (m, 9H, Ph), 7.72 (m, 4H, Ph), 7.83 (d, 2H, J = 7.0 Hz, Ph), 7.98 (s, 2H). Compound **11b**: ^{1}H NMR: 1.71 (d, 3H, J = 7.2 Hz, CH_3), 3.67 (s, 3H, OCH_3), 5.57 (q, 1H, J = 7.0 Hz, CHN), 7.56 (m, 9H, Ph), 7.83-7.94 (m, 6H, Ph), 7.99 (s, 2H).

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