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Acylation of Pyrrole and Investigation of Direct γ-Butyrolactone Reactions

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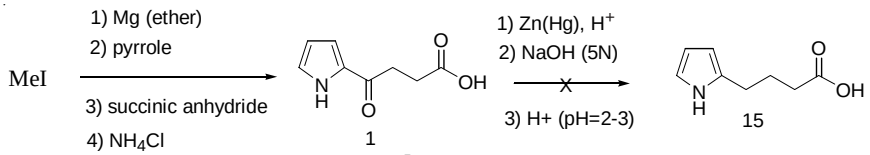
Selective acylation of pyrrole at two different sites (C_2, C_3) utilizing entirly different methods with good yield was achieved. The pre-formed 4-oxo-4-(1*H*-pyrrol-2-yl)-butyric acid (**1**) was taken for Clemmensen reduction and the reaction remained unchanged. The selected acylation at C_3 of pyrrole was prepared the regeoselectivity of the attack depending both on choices of catalyst and on the particular acylating agent. The pre-formed 4-oxo-4-[(1-phenylsulfonyl)-3-yl]-butyric acid was reduced through Clemmensen reduction led to the preparation of 4-(1*H*-pyrrol-3-yl)-butyric acid. Lactonization of this acid in the presence of $Na_2S_2O_8/CuCl_2$ system in H_2O at different temperatures was achieved.

Key Words: Selective acylation, Pyrrole, $Na_2S_2O_8/CuCl_2$ system, 4-(1*H*-pyrrol-3-yl)-butyric, Direct lactonization.

INTRODUCTION

Pyrrole derivatives have immense uses[1,2] as antibacterial, antifungal agents, pheromones, haem as an active site of the cytochromes and corrin in vitamin B_{12}.

Alkali metal salts of pyrrole are usually acylated on nitrogen, but Grignard reagents usually react to give 2-acyl derivatives[3]. In this study, selective acylation of pyrrole at two different sites (C_2, C_3) utilizing entirly different methods (**Schemes 1** and **2**) was achieved.

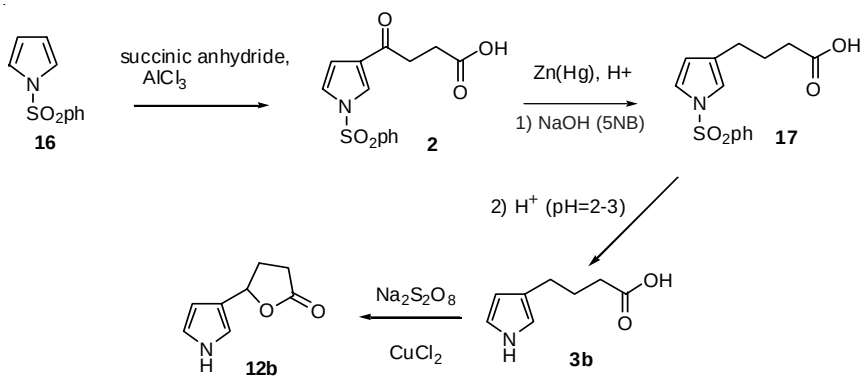


Scheme-1

The synthesized 4-oxo-4-(1*H*-pyrrol-2-yl)-butyric acid (**1**) was selectively taken for Clemmensen reduction for preparation of 4-(1*H*-pyrrol-2-yl) butyric acid (**15**). However, the reaction after 24 h reflux remained unchanged. In other effort, the selected acylation at C_3 of pyrrole was prepared *via* 1-phenylsulfonyl pyrrole. Acylation of 1-phenylsulfonyl

pyrrole with its deactivating N-substituent required more forcing conditions in the form of a Lewis acid as catalyst. The regeoselectivity of the attack depending both on choices of catalyst and on the particular acylating agent as illustrated in (**Scheme-2**)[4,5]. The preformed 4-oxo-4-[(1-phenylsulfonyl)-3-yl]-butyric acid (**2**) from acylation of (**16**) in the presence of succinic anhydride was reduced through Clemmensen reduction[6-8] followed by deprotection of phenylsulfonyl moiety, which after hydrolysis of (**17**) led to the preparation of 4-(1*H*-pyrrol-3-yl)-butyric acid (**3b**).

γ-Lactones are important synthetic intermediates found in several natural products and some drugs and have been synthesized by different methods[9-14]. Recently, a special mono and di-substituted γ-butyrolactones with aryl and aliphatic substitution at carbon 3,5 & 3,4 and 5 as an antiglaucoma, anti-tumour and an essence, respectively is reported[15-18].



Scheme-2

A general route has been established for direct conversion of several 4-substituted aryl acids[6] and *o*-alkyl aromatic carboxylic acids[7] in the presence of an oxidative system such as $S_2O_8^{2-}$, Cu^{2+} through stable benzyl radicals and benzyl cations. The present procedure presumably involves use of anchimeric assistance of 1,5-H-atom transfer reaction of benzilic system in aqueous solution at 85-90ºC. These reactions led to the formation of corresponding γ-butyrolactones from mild to high yields (25-85%) utilizing corresponding 4-substituted aryl acids[6] or *o*-alkyl aromatic carboxylic acids[7].

EXPERIMENTAL

Products were characterized using various techniques, *e.g.* IR, NMR, GC and TLC. Melting points are uncorrected and determined by Metller Fp5 melting point apparatus. IR spectra were obtained on a Shimadzu IR-470. All NMR data were recorded in $CDCl_3$ on Brucker Avance 500 MHz

spectrometer. Chemical shifts are reported in ppm (δ) using TMS as internal reference. Elemental analysis was performed at the Research Center of National Oil Co. Solvent reagents and chemical materials were purchased from Merck and Fluka and were used without further purification. The salts of dimethylamine hydrochloride, piperidine hydrochloride and diethylamine hydrochloride were prepared in our laboratory and their m.p. and IR were compared with literature.

Preparation of 4-oxo-4-(1*H*-pyrrol-2-yl)-butyric acid (1): To a flame-dried 250 mL three-neck round bottom flask equipped with an addition funnel and reflux condensor and under stream of an argon atmosphere was added 1.21 g (0.042 mol) of Mg powder. The reflux condenser equipped with $CaCl_2$ guard tube, 10 mL anhydrous diethyl ether was added to the round bottom flask. To this reaction mixutre, 0.5 mL portion of MeI (5.68 g, 0.04 mol, 2.49 mL) was added, if small bubbles formed at the surface of the Mg powder or if the mixture turn slightly cloudy or chalky, the reaction has started. The flask should become slightly warm. The rest of MeI was diluted with 15 mL anhydrous diethyl ether and was added to the reaction mixture dropwise from addition funnel during 0.5 h. The reaction mixture was reflux gently for 0.5 h and was cooled to room temperature. To this reaction system, 2.68 g (0.04 mol, 2.77 mL) fresh distilled pyrrole was added dropwise after 15 min and stirred for 10 min. After this time 4 g (0.04 mol) anhydride succinic was added to the flask during 0.5 h. The resulting solution was stirred for 4 h. After that the reaction solution was quenched by adding 30 mL 15% NH_4Cl. The organic phase was separated, the aqueous phase washed with 3 × 30 mL ether. The organic phases were combined together and active carbon was addded and filtered, dried over $MgSO_4$ and finally, the solvent evaporated under vacuum distilled. The resulting 5 mL ether solutions were cooled. The crude compound was washed with 2 × 10 mL CH_2Cl_2 and recrystallized from acetonitrile 0.72 g (10 %) m.p. 147-149ºC. IR (KBr, cm^{-1}) ν 3300 s, 1700 s, 1628 s, 1400 m, 1225 s, 1110 m, 760 m; ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.5 (q, J 6.5, 7.9 Hz, 2H, CH_2, H-3), 3 (t, J 6.5, 2H, CH_2, H-2), 6.1 (t, J 6.5 Hz, 1H, H-4'), 6.9 (dd, J 6.5 Hz, 1H, 2H, H-5'), 11.8 (s, 1H, NH), 12.1 (s, 1H, OH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 28 (C-2), 33 (C-3), 110 (C-4'), 116 (C-5'), 125 (C-3'), 132 (C-1'), 174 (C-4), 188 (C-1) ppm.

Preparation of 1-benzenesulfonyl-1*H*-pyrrole (16): To a 500 mL round bottom flask was added 150 mL THF (dry over sodium) and 13.83 mL 13.418 g (0.2 mol) freshly distilled pyrrole. To this reaction mixture, 7.036 g (0.18 mol) of potassium was slowly added. The resulting mixture was subjected for reflux until all potassium disappeared and the reaction completed. After cooling the reaction mixture added 100 mL THF and 19.19

mL (26.93 g, 0.15 mol) phenyl sulfonyl chloride in 150 mL anhydrous THF was added dropwise during 0.5 h. The solution was allowed to stir at room temperature for 14-18 h. The solution was filtered and the solvent was evaporated under vacuum. The crude crystal was recrystallized from MeOH. The white needle-like crystals 22.5g (73.3%) m.p. 89ºC (lit. 89-89.5)[19]. IR (KBr, cm^{-1}) ν 3100 m, 1450 m, 1360 s, 1170, 1185 s, 1080 s, 720 s; ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.3 (t, J 1.6 Hz, 2H), 7.2 (t, J 2.2 Hz, 2H), 7.5 (t, J 1.3Hz, 2H, ArH), 7.6 (q, 1H, ArH), 7.8 (d, 2H, ArH) ppm.

Preparation of 4-(1-benzenesulfonyl-1*H*-pyrrol-3-yl)-4-oxo-butyric acid (2): To a 500 mL oven-dried flask 21.26 g (0.16 mol) $AlCl_3$ and 290 mL 1,2-dichloroethane was added. To this solution, 7.98 g (0.08 mol) succinic anhydride was added at 25ºC. The resulting mixture allowed to stirred for 20 min, until all of the anhydride was dissolved. To this flask, 15 g (0.07 mol) of 1-(phenyl sulfunyl)pyrrole (**16**) was added in 40 mL 1,2-dichloroethane and finally the resulting mixture was allowed to stirred for 1.5 h at 25ºC. To this resulting mixture 100 mL of CH_2Cl_2 was added. The organic layer transferred into a separatory funnel, washed with distilled water. The two organic phases were combined, dried over $MgSO_4$ and the solvent evaporation give 17 g (76.4 %) of solid, recrystalized from CH_2Cl_2. The resulting pure crystals had a weight of 10.68 g (48%, yield) m.p. 126ºC (lit. 124-126ºC)[20]. IR (KBr, cm^{-1}) ν 3300-2500, 1695 s, 1670 s, 1365 s, 1170 s, 1185 s, 1085 s, 730 s. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.7 (t, J 6.6 Hz, 2H, H-2), 3 (t, J 6.6 Hz, 2H, H-3), 6.7 (dd, J 1.6 Hz, 1H, H-4') 7.1 (dd, J 2.2 Hz, 1H, H-5'), 7.5 (t, J 7.5 Hz, 2H, H-3'), 7.6 (s, J 1.83 Hz,1H, ArH), 7.8 (t, J 1.87 Hz, 1H, ArH), 7.9 (dd, J 1.3Hz, 2H, ArH), 10.8 (s, 1H, OH) ppm.

Preparation of 4-(1-benzenesulfonyl-1*H*-pyrrole-3-yl)butyric acid (17): 45.8 g (703 mmol) Zn powder, 4.58 g (16.82 mmol) mercury(II) chloride, 3 mL conc. HCl and 60 mL distilled water, were placed in a 500 mL flask. The mixture was stirred at room temperature for 20 min to produce a homogenous solution. After homogenization, the liquid was decanted as completely as possible. In a flask equipped with reflux condenser, 30 mL distilled water, 66 mL conc. HCl, 300 mL toluene and 14.71 g (48 mmol) 4-(1-benzenesulfonyl-1*H*-pyrrole-3-yl)-4-oxo-butyric acid (**2**) were placed. The flask was refluxed vigorously for 20 h. During this period 3 × 25 mL conc. HCl was added to the flask at *ca*. 6 h intervals in order to maintain the conc. of HCl. After cooling two layers were separated. The aqueous layer was extracted with 3 × 30 mL ether, the extracted layer was added to toluene, washed with water and dried over $MgSO_4$. The solvent was evaporated and the residue was recrystallized with toluene to afford a 17, 10 g (71.4%) of crystal m.p. 94ºC (lit. 91-93ºC)[20]. IR (KBr, cm^{-1}) 3360

m, 3200-2500, 1690 s, 1365 s, 1180 s, 1170 s, 1080 s, 730 s; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.7 (m, 2H, H-3), 2.1 (t, J 7.4 Hz, 2H, H-2), 2.3 (t, J 7.65 Hz, 2H, H-4), 3.3 (s, 1H, H_2O), 6.2 (t, J 1.6 Hz, 1H, H-4'), 7.1 (s, 1H, H-2'), 7.2 (s, 1H, H-3'), 7.6 (t, J 7.8 Hz, 2H, ArH), 7.7 (t, J 7.5Hz,1H, ArH), 7.9 (s, 2H, ArH),12 (s, 1H) ppm.

Preparation of 4-(1*H*-pyrrol-3-yl)-butyric acid (3b): To a 250 mL flask, 7 g (0.024 mol) 4-(1-benzenesulfonyl-1*H*-pyrrole-3-yl)-butyric acid (**17**) acid and 85 mL of 1,4-dioxane were placed. The reaction mixture was stirred to produce a homogenous solution. To this solution, 70 mL of NaOH (5N) was added drop wise and subjected to gentle stirring at room temperature for 18 h. The pH of the solution was adjusted to 2 by carefully adding HCl (6N). The aqueous layer was separated and then extracted with (3 × 30 mL) diethyl ether. The organic layers were combined, washed with saturated solution of brine and water and dried over $MgSO_4$. The solvent was evaporated under reduce pressure. Tha residue was recrystallized with toluene, 3.07 g (84%) white needle-like crystal of (**3b**) was recoverd mp 91-92ºC (lit. 93-94ºC). IR (KBr, cm^{-1}) 3390 s, 3200-2500, 1685 s, 1430 m, 1280 m, 1190 m, 765 s; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.7 (m, 2H, H-3), 2.2 (t, J 7.4 Hz, 2H, H-2), 2.3 (t, J 7.6 Hz, 2H, H-4), 3.3 (s, 1H, H_2O), 5.8 (d, J 1.7Hz, 1H, H-4'), 6.5 (s, 1H, H-2'), 6.6 (dd, J 2.3 Hz, 1H, H-5'), 10.4 (s, 1H, H-1'), 11.9 (s, 1H, OH), ppm.

Preparation of 4-oxo-4-[1*H*-pyrrol-3-yl]butanoic acid (18): A similar procedure was followed as used for preparation of (**3b**) from (**17**) was applied to compound (**2**). The crude product was recrystalized from EtOAc. The white precipitate of (**18**) 3.1 g (67.4%), m.p. 167ºC. IR (KBr, cm^{-1}) 3360 m, 3200-2500 b, 1725 s, 1615 s, 1610 s, 1410 m, 1230 s, 1135 s, 745 m, 600 m; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.5 (t, J 6.25, 6.7 Hz, 2H, H-2), 2.9 (t, J 6.35, 6.75 Hz, 2H, H-3), 6.4 (s, 1H, H-4'), 6.8 (s, 1H, H-5'), 7.5 (t, 1H, J 1.2, 1.45 Hz, H-2'), 11.4 (s, 1H, NH), 12 (s, 1H, OH) ppm.

Prepration of 5-(1*H*-pyrrol-3-yl)-dihydro-furan (12b): 1 g (6.5 mmol) of 4-(1*H*-pyrrol-3-yl)butanoic acid (**3b**), 10 mL distilled water and 1.12 g (6.5 mmol) $CuCl_2.2H_2O$ were combined in a 100 mL two-necks round bottom-flask. The colour of solution turn to deep brown. It looks like that the pyrrole oxidized at this condition in the presence of $CuCl_2$ and $Na_2S_2O_8$. The flask was equipped with a reflux condenser and an additional funnel. Solution of 1.56 g (6.5 mmol) $Na_2S_2O_8$ and 5 mL water were added to the additional funnel. The reaction mixture was allowed to reflux by vigorous stirring while the temperature of solution was adjusted to 85-90ºC. The solution was added dropwise to a flask during 40 min and the flask was refluxed for 3.5 h. After this time the reaction was stopped. The flask was cooled and extracted with 3 × 15 mL ether and dried with $MgSO_4$.

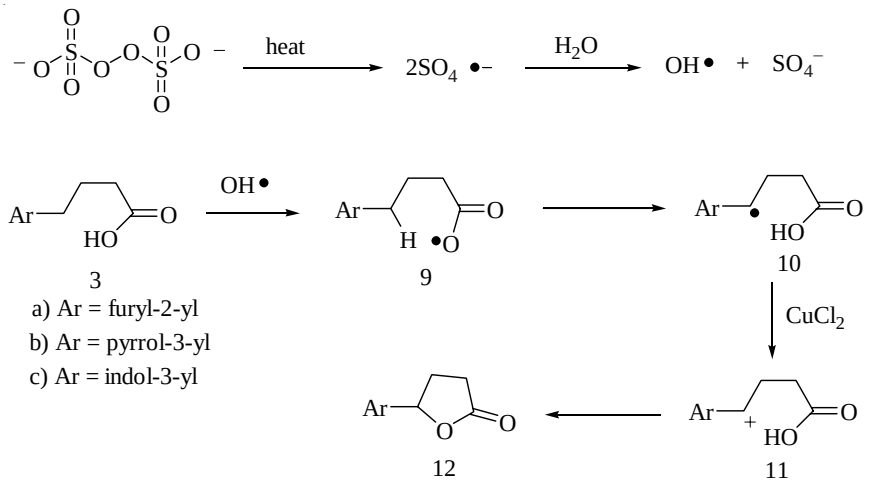
The solvent was removed. The IR of the crude product semi-viscous solid recoverd 1.6 g showed the (C=O) stretching band as a sholder at 1760 cm^{-1} and apparently polyalkylated polymeric by-products was recovered. IR (KBr, cm^{-1}) 3200 m, 3050 (shoulder), 1760 s, 1700 vs, 1625 s, 1475 s, 1290 s, 1190 s, 850 s, 690 m; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25-2.34 (m, 4H, 2 × CH_2), 5.8 (d, J 1.7Hz, 1H, H-5), 6.5 (s, 1H, H-4'), 6.6 (dd, J 2.3 Hz,1H, H-5'), 7.4 (t, 1H, J 1.2, 1.45 Hz, H-2'), 10.4 (s, 1H, NH), ppm.

Preparation of 4-oxo-4-(1*H*-pyrrol-3-yl)-butyric acid ethyl ester (13): To a 100 mL flask, 1.66 g (0.01 mol), 4-oxo-4-(1*H*-pyrrol-3-yl)-butyric acid (**18**), 20 mL anhydrous ethanol and 30 mL solution dry freshly distilled benzene were added. To the resulting solution, 3 mL H_2SO_4 (98%) was added dropwise and stirred. The flask was equipped with reflux condensed and refluxed for 6 h. The progress of the reaction was monitored with TLC. After cooling to room tempreture, 300 mL water was added to the flask, two layers were separeted with (3 × 30 mL) diethyl ether. The extracted layer was added to benzene, washed with saturated $NaHCO_3$ and dried over $MgSO_4$, decolorized with active carbon. Two-third of the solvent was evaporated. The remaining solution was cooled to afford 1.37 g (69.8%), white crystal, m.p. 89-91ºC. IR (KBr, cm^{-1}) 3250 s, 1715 s, 1625 s, 1405 m, 1370 m, 1210 m, 1165 m, 770 m, 600 m; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.2 (t, J 7.1 Hz, 3H, CH_3), 2.7 (t, J 6.83, 2H, H-2), 3.1 (t, J 5.6, 6.9 Hz, 2H, H-3), 4.1 (q, J 7.1Hz, 2H,CH_2-CH_3), 6.6 (d, J 1.5 Hz, 1H, H-4'), 6.7 (dd, J 2.1, 2.3 Hz, 1H, H-5'), 7.4 (t, J 1.3 Hz, 1H, H-2'), 9.2 (s, 1H, NH) ppm.

Preparation of 5-(furan-2-yl)-dihydrofuran-2(3*H*)-one (12a): 0.45 g (3 mmol) 4-furan-2-yl-butyric acid (**3a**), 13 mL distilled water and 0.51 g (3 mmol) $CuCl_2.2H_2O$ were placed in a 100 mL two-necks round bottom flask. The flask was equipped with a reflux condenser and an additional funnel. Solution of 0.85 g (3 mmol) $Na_2S_2O_8$ and 2 mL water were added to the additional funnel. The reaction mixture was allowed to reflux by vigorous stirring while the temperature of solution was adjusted to 85-90ºC. The solution from additional funnel was added dropwise to a flask during 40 min and the flask was refluxed for 3.5 h. The flask was cooled and extracted with (3 × 3 mL) ether and dried with $MgSO_4$. The solvent was removed and 0.21 g (49 %) was collected as a pure center cut from preparative chromatography. Anal. for $C_8H_{10}O_3$ calcd. (found) %: C 63.15 (63.20), H 5.26 (5.20). IR (KBr, cm^{-1}) 2900 w, 1760 s, 1460 m, 1100 m. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.3-2.39 (m, 4H, 2 × CH_2), 5.8 (t, J 7.5 Hz, 1H, H-5), 6.6 (s, 1H, H-3'), 7.2 (s, 1H, H-4'), 7.6 (s, 1H, H-5').

RESULTS AND DISCUSSION

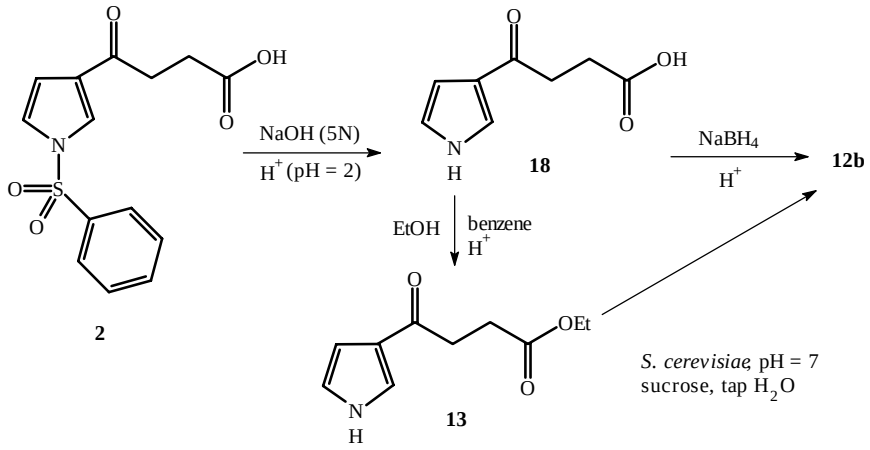
In continuation to our previous studies, the related 4-pyrrole-3-yl-butyric acid (**3a**), 4-furan-2-yl-butyric acid (**3b**) and 4-(1*H*-indol-3-yl)-butyric acid (**3c**), the order of stablity of radicals simply base on the yield % of recovered lactones was found to be (**3a**) > (**3b**) > (**3c**). Theses reactions mediated by benzylic radical (**10)** and consequently cation **11** in aqueous intermediate in reasonable yields (**Scheme-3**). The furyl-2-yl-, pyrrol-3-yl and indol-3-yl butyric acids (**3a**), (**3b**) and (**3c**) were prepared from accessible starting materials by applying straight forward procedures. Lactonization of 4-(1*H*-pyrrole-3-yl)-butyric acid (**3b**) in the presence of $Na_2S_2O_8$ / $CuCl_2$ system in H_2O at different temperatures 40, 50, 60, 70, and 90ºC was achieved. However, at 90ºC the yield of lactonization product (**12b**) was less than (**12a**) (IR of the crude product showed C=O stretching bond at 1760 cm^{-1}). The major reason for the low yield of lactone is due to the formation of a polymeric byproduct in substantial quantities.



(Scheme-3)

Reproduction of this procedure to (**3c**) provided (**12c**) in low yield. In the other attempt the precursor 4-oxo-4-(1*H*-pyrrole-3-yl)-butyric acid (**3**) was taken for selectively reduction with $NaBH_4$ over 20 h and hydrolysis with dilute acid over night to provide the corresponding γ-acid alcohol which could after work-up, spontaneously cyclized to desired lactone (**12b**), however the reaction was failed (**Scheme-4**).

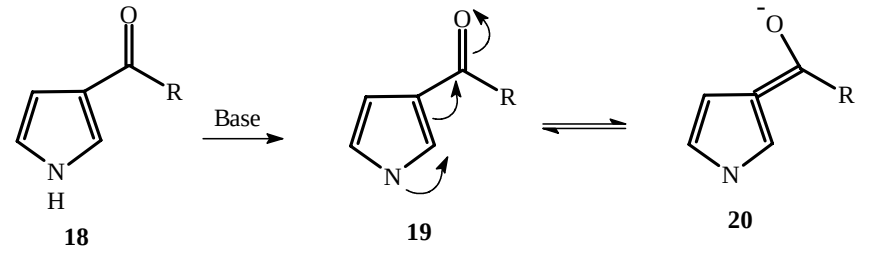
In an alternative experiment, precursor keto acid (**3**) was converted to the corresponding ethyl ester (**13**), purified and characterized by spectroscopic methods. The enantioselective reduction of ethyl-4-oxo-(1*H*-pyrrole-3-yl)-butanoate (**13**) in the presence of *S. cerevisiae* (baker's yeast) for 175 h to prepare chiral lactone (**12b**) was also failed (**Scheme-4**).



Scheme-4

Conclusions

The acylation of pyrrole selectively at two different sites (C_2, C_3) employing two different methods with good yield was achieved. The preformed 4-oxo-4-(1*H*-pyrrole-2-yl)butyric acid (**1**) was taken for Clemmensen reduction the reaction remained unchanged. This complexity was solved by preparation of 4-oxo-4-[(1-phenylsulfonyl)-3-yl]butyric acid (**2**) from acylation of (**16**) in the presence of succinic anhydride. The deprotection of phenylsulfonyl moiety, after hydrolysis of (**17**) led to the preparation of 4-(1*H*-pyrrol-3-yl)butyric acid (**3**). The failure of carbonyl group reduction of (**18**), could be attributed to the N-H acidity of pyrrole ring containing electron-withdrawing group such as acyl at C_3 position. The deloclization of the lone pair in pyrrole (**19**) could be described by charge-separated resonance forms as shown in (**Scheme-5**). In consequence the (C=O) group is likely to remains predominately as a single bond (**20**). Further investigation desired to increase the yield for lactone (**12b**) and (**12c**). This procedure for prepration of lactone (**12a**) works exceptionally well.



R = $-CH_2CH_2COOH$

Scheme-5

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